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PB-276 155

Current Status of Alternative Automotive Power Systems and Fuels. Volume III Alternative Nonpetroleum-Based Fuels

Aerospace Corp, El Segundo, Calif Environmental Programs Group

Prepared for

Environmental Protection Agency, Ann Arbor, Mich

Jul 74

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CURRENT STATUS OF ALTERNATIVE AUTOMOTIVE POWER SYSTEMS AND FUELS

VOLUME III - ALTERNATIVE NONPETROLEUM-BASED FUELS

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Mobile Source Air Pollution Control
Alternative Automotive Power Systems Division
Ann Arbor, Michigan 48105

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-460/3-74-013-c

2.

3. RECIPIENT'S ACCESSION NO.
PB276155

4. TITLE AND SUBTITLE
Current Status of Alternative Automotive Power Systems and Fuels
Volume III - Alternative Nonpetroleum-Based Fuels

5. REPORT DATE
July 1974

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NO.
ATR-74(7325)-1, Vol. III

9. PERFORMING ORGANIZATION NAME AND ADDRESS
The Environmental Programs Group
Environment and Urban Division
The Aerospace Corporation
El Segundo, Calif. 90245

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
68-01-0417

12. SPONSORING AGENCY NAME AND ADDRESS
EPA, Office of Air and Waste Management
Office of Mobile Source Air Pollution Control
Alternative Automotive Power Systems Division
Ann Arbor, Michigan 48105

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A summarization has been made of the available nonproprietary information on the technological status of automotive power systems which are alternatives to the conventional internal combustion engine, and the technological status of non-petroleum-based fuels derived from domestic sources which may have application to future automotive vehicles. The material presented is based principally upon the results of research and technology activities sponsored under the Alternative Automotive Power Systems Program which was originated in 1970. Supplementary data are included from programs sponsored by other government agencies and by private industry. The results of the study are presented in four volumes; this volume presents available information pertaining to alternative nonpetroleum-based automotive fuels.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Automotive Nonpetroleum-Based Fuels, Synthetic Gasoline and Distillate Hydrocarbons, Methanol, Methane, Propane and Butane, Ethanol, Hydrogen, Ammonia, Hydrazine, Fuels Reformed On-Board Vehicle	Characterization, Production Processes Engine/Vehicle Compatibility Technology Status Domestic Resources Consumer Costs Capital Costs	

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 363
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE PCA16 - A01

EPA Form 2220-1 (9-73)

EPA-460/3-74-013-c

CURRENT STATUS OF ALTERNATIVE AUTOMOTIVE POWER SYSTEMS AND FUELS

VOLUME III - ALTERNATIVE NONPETROLEUM-BASED FUELS

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The Environmental Programs Group

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Contract No. 68-01-0417

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Mobile Source Air Pollution Control
Alternative Automotive Power Systems Division
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July 1974

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This report was furnished to the U. S. Environmental Protection Agency by the Aerospace Corporation, El Segundo, California, in fulfillment of Contract No. 68-01-0417 and has been reviewed and approved for publication by the Environmental Protection Agency. Approval does not signify that the contents necessarily reflect the views and policies of the agency. The material presented in this report may be based on an extrapolation of the "State-of-the-art". Each assumption must be carefully analyzed by the reader to assure that it is acceptable for his purpose. Results and conclusions should be viewed correspondingly. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Publication No. EPA-460/3-74-013-c

FOREWORD

This report, prepared by The Aerospace Corporation for the Environmental Protection Agency (EPA), Alternative Automotive Power Systems Division, summarizes available nonproprietary information on the technological status of automotive power systems which are alternatives to the conventional internal combustion engine, and the technological status of nonpetroleum-based fuels derived from domestic sources which may have application to future automotive vehicles.

The status of the technology reported herein is that existing at the end of 1973 with more recent data in selected areas. The material presented is based principally upon the results of research and technology activities sponsored under the Alternative Automotive Power Systems (AAPS) Program which was originated in 1970 and which is administered by the Alternative Automotive Power Systems Division of EPA. Supplementary data are included from programs sponsored by other government agencies and by private industry. Additional information on technology and development programs is known to the government but cannot be documented herein because the data are proprietary.

One purpose that the AAPS Program serves is to provide a basis of knowledge and perspective on what can and cannot be accomplished with the use of alternative propulsion and fuels technology and to disseminate this information to Congress, Federal policy makers, industry, and the public. Thus, the publication of information such as that contained herein is in keeping with this element of the mission of the AAPS Program. This is the first of a series of reports on alternatives that are intended to be published annually.

The results of this study are presented in four volumes and three main topical areas:

Volume I. Executive Summary
Volume II. Alternative Automotive Engines

Volume III. Alternative Nonpetroleum-Based Automotive Fuels

Volume IV. Electric and Hybrid Power Systems

Volume I, the Executive Summary, presents a concise review of important findings and conclusions for all three topical areas. Thus, an overview of study results may be obtained by reading Volume I only. Volumes II, III, and IV contain detailed, comprehensive discussions of each topical area and are therefore of interest primarily to the technical specialist. Each of these three volumes also contains Highlights and Summary sections pertaining to the topical area covered in the volume.

This volume, Volume III, presents available information pertaining to the current technological status of alternative nonpetroleum-based automotive fuels which may have application to future energy demands imposed by automotive vehicles.

A brief review of important findings and conclusions is presented in the Highlights and Summary sections. A short overview of energy supply/demand trends and the implications of the United States self-sufficiency goal is given in Section 1. Section 2 presents an overview of energy resources for transportation needs and industry projections for meeting them. Sections 3 through 11 address in detail the available data concerning the potential use of the following types of alternative automotive fuels: synthetic gasoline and distillate hydrocarbons, methanol and methanol-gasoline blends, methane (natural gas and synthetic natural gas), propane and butane, ethanol and ethanol-gasoline blends, hydrogen, ammonia, hydrazine, and fuels reformed on-board conventional gasoline engine-powered automobiles. Principal topics covered for each alternative fuel are characterization, suitability for use as an engine fuel, current status, and projected status.

ACKNOWLEDGMENTS

Appreciation is acknowledged for the guidance and assistance provided by Mr. Graham Hagey of the Environmental Protection Agency (EPA), Alternative Automotive Power Systems (AAPS) Division, who served as EPA Project Officer for this study. Appreciation is also extended to staff members in the AAPS Division, to other EPA divisions, to various government agencies, and to those in industry and the academic community who supplied reference material and reviewed the contents of this report.

Data provided by Exxon Research and Engineering Company and the Institute of Gas Technology were derived from the study effort performed by them under contract to AAPS/EPA.

The following technical personnel of The Aerospace Corporation made valuable contributions to the effort performed under this contract:

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HIGHLIGHTS

Several nonpetroleum-based alternative fuels derived from domestic sources have been considered as potential replacements for, or partial supplements to, conventional petroleum-based gasoline and distillate fuels for automotive use. Based on data sources in the open literature and on information provided by Exxon Research and Engineering Company and the Institute of Gas Technology (IGT) during their study contracts with EPA, a status review of these fuels has been conducted with particular emphasis on requirements of the personal passenger car in a near-term period (1975 to 1985)* and in a far-term period (1985 to 2000). The fuels that were examined consisted of: synthetic gasoline and distillate hydrocarbons, methanol and methanol-gasoline blends, methane (synthetic natural gas), propane, ethanol and ethanol-gasoline blends, hydrogen, ammonia, and hydrazine. In addition, the concept of reforming fuels (chemical conversion) in a gas generator on the vehicle was also considered.

The evaluation of each fuel was predicated on numerous interacting factors, among which were abundance of domestic resources, technological status of production techniques, schedule for mass production, estimated capital and consumer costs, and adaptability to both internal and external combustion types of engines for automobiles (including characteristics related to fuel economy, exhaust emissions, handling, storage, and toxicity). It is noted that evaluations relating the ability of nonpetroleum-based alternative fuels to compete in price with petroleum-based fuels are in a state of flux because of the recent fluctuations in the cost of automotive fuel. Likewise, cost estimates for alternative fuels may be revised as more data are acquired from future pilot and prototype demonstration fuel production plants.

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*Exxon and Institute of Gas Technology designations were: near term (1975-1985), mid-term (1985-2000), and far term (beyond 2000).

It should also be recognized at the outset that an important factor affecting the rate of possible implementation of each of these fuels (except synthetic gasoline and distillate fuels) would be the need for a completely new nationwide specialized distribution and storage network. Undoubtedly, if they were introduced, a dual-fuel system would be required for an extended period of time to satisfy the needs of both gasoline-fueled vehicles and new vehicles designed to use the alternative fuel.

Based on all the aforementioned considerations, it would appear that synthetic gasoline and distillate hydrocarbons manufactured from coal and shale will offer the greatest promise for contributing to automotive fuel requirements in both the near-term and far-term periods. Coal-derived methanol, particularly in a methanol-gasoline blend, could be considered a secondary fuel source if certain technical problems can be solved. Another alternative fuel of merit is hydrogen, but it can only be considered as a significant contributor to automotive needs in the period beyond the year 2000. The rationale for these selections is amplified in the following highlights which present the essential elements of the current status of alternative automotive fuels.

Synthetic Gasoline and Distillate Hydrocarbon Fuels

1. Synthetic gasoline and distillate hydrocarbon fuels could be manufactured from coal, oil shale, tar sands, or organic waste products. They possess the primary advantage of expected complete compatibility with existing and advanced automotive power plants, as well as with distribution facilities down to the local gas station.
2. Coal (particularly from strip mining processes) is by far the largest and most probable domestic energy resource available for synthetic fuel production, followed by oil shale. Additional domestic sources of much less potential, in terms of ability to meet projected energy needs, are tar sands and organic waste products.
3. The production cost in the post 1985 time period for gasoline and distillate hydrocarbon fuels derived from oil shale is estimated to be competitive with that for current costs of conventional petroleum-based sources. Equivalent liquid hydrocarbon fuels derived from coal are more expensive but are

also competitive. Waste product disposal constitutes a serious environmental problem in either case with processed oil shale being the most critical concern.

4. The production economics for liquid hydrocarbon fuels derived from coal and shale will ultimately depend on (a) the efficient commercialization of various production processes currently under evaluation in laboratory and pilot-plant models, and (b) the transport distance required for raw and/or refined products. Intensive capital investment will be required if several 50,000- to 100,000-barrel-per-day plants are to be in operation in the 1980-1985 period.

5. Little information is available on the actual use of synthetic gasoline or distillates in automotive engines. A test program to verify the compatibility of these fuels with automotive engines is planned for Fiscal Year 1975 under an interagency agreement between EPA and the Bureau of Mines.

Methanol and Methanol-Gasoline Blends

1. Pure methanol has seen limited successful use with spark ignition engines powering automobiles. It offers the following advantages:
    a. An increase in power from existing engines fueled with gasoline, largely because methanol heat of vaporization characteristics lead to increases in air inducted into the engine and to increases in net work output.
    b. An increase in efficiency and in power output per pound of engine weight for new engine designs because the engine can operate at higher compression ratios than with high octane premium gasoline.
2. Certain disadvantages of pure methanol will require that careful preparation by fuel distributors and automotive manufacturers precede its possible introduction into the retail sales market. Among these disadvantages are:
    a. Fuel economy (in miles per gallon) with pure methanol is about half that with gasoline, necessitating a major increase in the size of the automobile fuel tank and modifications to the carburetor fuel jets [although the energy expended each mile (in Btu per mile) in powering an automobile with methanol is equivalent to the energy expended with gasoline].
    b. When contrasted with gasoline, vapor pressure characteristics of pure methanol imply that there may be a greater incidence of vapor lock with current automobile

fuel system designs. Also, cold start is more difficult and manifold preheating is required to ensure complete vaporization in carbureted systems.

c. Miscibility between pure methanol and water can result in the presence of water (from local atmospheric moisture condensation) in the fuel distribution system, in the service station tanks, and in the vehicle tank, leading to possible corrosive action on metal surfaces in piping, tankage, and within the engine itself. Corrosion inhibitors may be required in the fuel to avoid this problem.

d. Synthetic methanol transport costs are expected to be higher than those estimated for synthetic gasoline because, for equal energy content, the pure methanol volume required to be piped, trucked, and stored is approximately twice that of gasoline. Therefore, when distribution costs are included, the cost at the pump to the consumer, per unit of fuel energy delivered (excluding tax), is estimated to be 10 to 30 percent greater than that for synthetic gasoline from coal and shale,respectively.

e. The solvent action of pure methanol may damage paint, metal, and plastic surfaces; therefore, solvent-resistant materials must be considered for use in all applications.

3. A greater near-term advantage may be evident by the use of methanol-gasoline blends rather than pure methanol. This approach would conserve gasoline stocks to a small degree without necessitating major redesign of automobiles or engines. It should be noted, however, that even if methanol is added in a methanol-gasoline blend only to the five percent level, current automotive fuel consumption would require about five times the present U.S. methanol production.

4. As with pure methanol, methanol-gasoline blends have a higher octane rating than gasoline alone. But there are indications that the motor octane number (MON) increase is not nearly as great as that which would be expected from measured increases in the research octane number (RON). This would indicate that engine road performance increases will not be as marked as those found in the laboratory.

5. Vapor lock and water miscibility problems would be present to a much greater degree with methanol-gasoline blends than with pure methanol. An example of these problems is the separation of gasoline and methanol in the presence of very small amounts of water, particularly at low temperatures. Solutions to these problems may be possible, but they require laboratory and road test verification.

6. The majority of published data on the application of methanol and methanol-gasoline blends to fueling automotive engines is about 20 to 30 years old. The use of new materials, engines, gasoline blends, and lubricating oils is a compelling factor for acquiring more contemporary characteristics of methanol in order to verify or invalidate older concepts regarding advantages and disadvantages of this alternative fuel. In this regard, the adaptability of methanol and methanol-gasoline blends to modern automotive systems will be explored systematically in a test program initiated by the Bureau of Mines through an interagency agreement with EPA. Other research programs investigating methanol and methanol blends are in progress or planned at several universities and industry research laboratories.

Methane (Synthetic Natural Gas)*

1. Because of supply constraints of natural gas, efforts are under way to develop the technology for deriving synthetic natural gas from either coal or liquid hydrocarbons. Production levels will depend on the completion of coal gasification plants which are first expected to be in operation in the post-1980 period.
2. Liquefied gas (natural or synthetic) is more attractive than the gaseous form because of its greatly increased density (resulting in reduced storage volume requirements in the vehicle). However, the low boiling point requires application of cryogenic tank insulation techniques which add substantially to automobile tankage weight and cost relative to a conventional gasoline system.
3. Energy expenditure per mile in powering an automobile with an engine converted to operate on natural gas is approximately equal to or better than that for a similar vehicle using a modern gasoline engine equipped with emission control devices. In general, exhaust emissions with natural gas are expected to be lower than those with gasoline.
4. A significant factor in the use of natural gas in place of gasoline as an automotive fuel is the reduced activity of hydrocarbon emissions in the formation of photochemical smog. Total hydrocarbon activity is four to six times less than that of gasoline.

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*Also referred to as Substitute Natural Gas

5. Because of the difficulties in implementation of an adequate fuel distribution system throughout national urban areas, and because of the problems of storage on the vehicle, neither liquified nor compressed natural gas is considered to be a primary alternative fuel candidate for large-scale automotive use. Usage would be expected primarily for commercial fleet operations. However, synthetic natural gas may be expected to be of significance in replacing petroleum fuels for stationary electric generating power plants based on projections that, in the far-term period, 20 to 25 percent of the total gas supply may come from coal gasification.

Propane

1. Propane appears suitable for use in all of the conventional and alternative engines currently being considered. Vehicle tankage volume and weight is less than that required for methane, and cryogenic cooling is not required for storage in a liquid form if the fuel is pressurized to about 250 pounds per square inch. However, as in the case of methane, this fuel is not considered a primary alternative candidate for large-scale automotive use because of distribution and storage problems.
2. Exhaust emissions from propane show marked reductions when compared to those from gasoline, but fuel economy trends are inconsistent amongst different data sources.
3. Adequate availability of the fuel is a major problem because the major production source of propane is natural gas processing plants (a declining resource). Hence, a new raw material source (e. g. , coal or oil shale) and production process would be required to increase its availability.
4. Consumer costs of liquid petroleum gas are generally similar to the price of gasoline, as of mid-1973, but gasoline is cheaper on the basis of energy expended per mile in powering an automobile. Furthermore, if in the future propane is manufactured synthetically from coal, costs to the consumer are projected to be greater than for synthetic methane (and certainly greater than for synthetic gasoline).

Ethanol and Ethanol-Gasoline Blends

1. Ethanol has been demonstrated to be compatible as a motor fuel with present vehicles. In many parts of the world, it has been blended in concentrations varying between 10 and 20 percent to alleviate gasoline shortages. Pure ethanol or blends with gasoline have essentially the same usage problems cited for methanol.

2. The economics and instability in the price of ethanol production based on fermentation of agricultural raw materials and the poor fuel economy are additional major factors tending to limit its use. Ethanol-gasoline blends have been considered, but the cheaper and equally efficient methanol-gasoline blends are preferred.

Hydrogen

1. Success has been attained in carrying out the necessary mechanical conversions to enable conventional gasoline engines to operate on hydrogen. Indications are that extremely low exhaust emission levels are possible. Fuel economy on an energy-expended-per-mile basis is found to be comparable to that for gasoline, but maximum engine power output for a given engine size is reduced significantly.
2. A major technical drawback with hydrogen, as fuel for the automobile, is the problem of storage on the vehicle. In compressed gas form it is not practical, and even in cryogenic liquid form the complex and expensive storage requires a tank capacity three and one-half times that needed for gasoline on an equivalent energy basis. Research is under way to evaluate an alternative reduced-volume storage approach using metal hydrides; a means of also reducing the storage weight will be necessary before this technique can be considered practical.
3. Additional major obstacles to using hydrogen as a universal fuel concern the energy supply adequacy for its manufacture as well as very high costs to the consumer. Nuclear power will be a necessary factor in ensuring an adequate supply of energy for production of hydrogen by water electrolysis. On an equivalent energy basis, liquid hydrogen cost to the consumer will be much greater than the cost of gasoline or distillate derived from coal. Much of this cost is attributable to significant cost items connected with the liquefaction of hydrogen and its subsequent transportation to, and storage at, retail outlets.
4. Even if costs are reduced, hydrogen appears to be a possible fuel only for the post 2000 time period. The massive capital requirements for manufacturing plants and distribution facilities, and the extensive period needed for actual construction activities, preclude any earlier consideration of this fuel as a major contributor to passenger car needs.

Ammonia

1. The interest in ammonia as an engine fuel stems from the consideration that it allows the storage of hydrogen in nitrogen hydride form at relatively low pressures without some of the fire and explosion hazards associated with pure hydrogen. But the extreme toxicity of ammonia, combined with expected high consumer costs, does not hold much promise for this fuel even for the far-term period.

Hydrazine

1. For the very same reasons cited for ammonia, hydrazine is considered unsuitable as an alternative to petroleum-based fuels.

Fuels Reformed On the Vehicle

1. One approach which is being investigated as a means of extending the lean operating limits of gasoline engines in order to achieve low exhaust emissions is the incorporation of a fuel reformer device to chemically convert all or a portion of the engine's fuel requirements from gasoline (or any liquid hydrocarbon fuel) to a gaseous product (principally hydrogen) prior to induction into the engine. Initial exploratory tests have indicated marked reductions in carbon monoxide and oxides of nitrogen exhaust emissions at very lean air-fuel ratios, but these positive factors are offset by high hydrocarbon exhaust emissions. Fuel economy is projected by some investigators to be equal to or better than that obtainable with a gasoline-powered engine.

2. Fuel-reformer concepts are still in the exploratory, proof-of-principle, or feasibility determination stage. A number of critical data gaps must be filled before the potential of reformed fuels can be fully assessed. NASA has been funding the Jet Propulsion Laboratory to acquire data and prove concept feasibility, and EPA is providing supplemental funding for this work in addition to other contractor-supported programs for evaluation of similar concepts.

SUMMARY

S. 1 SUMMARY OF ALTERNATIVE NONPETROLEUM-BASED FUEL RESOURCES

Domestic liquid petroleum products satisfied 74 percent of the United States energy consumption in 1971; they are expected to satisfy only about 1/2 of the need in the year 1985 and less than half in the year 2000. This excess demand-versus-supply situation provides a strong motivation for government agencies and the transportation industry (which consumes at present about 55 percent of liquid petroleum products) to investigate the potential of alternative nonpetroleum-based fuels for automotive applications. Several nonpetroleum-based alternative fuels have been considered as potential replacements for, or partial supplements to, conventional petroleum-based fuels. These were evaluated on the basis of: availability, compatibility with existing distribution and storage systems (both mobile and stationary), suitability for use with personal passenger cars, relative advantages in terms of vehicle fuel economy and emissions, costs to the consumer, capital investment costs, critical research gaps, technological status, and the time scale for production implementation. A principal data source used was the two EPA/AAPS-funded studies (with the Institute of Gas Technology and Exxon Research and Engineering Company) related to the assessment of alternative automobile fuels.

In evaluating the potential of alternative fuels for transportation, the energy source from which they are derived is a prime consideration. Sources available in the future will be coal, oil shale, solar energy, and nuclear energy, while liquid petroleum and natural gas will be in continued short supply. Significant production of liquid petroleum fuels from coal, oil shale, and tar sands cannot be expected until the far term period of 1985 to 2000.* Contributions to domestic energy needs from solar and nuclear energy are not expected to be available until even later periods.

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*Exxon and IGT designations were near term (1975-1985), mid-term (1985-2000), and far term (beyond 2000).

Coal is relatively plentiful in the U.S., but its availability will be somehow limited by the mining rate. The various forecasts which may require updating now show that it is possible to achieve a rate of domestic coal supply such that, after providing for its normal usage and for coal liquefaction and gasification, a surplus may be left allowing for coal export. Figure S-1 shows the forecast of the future coal supply and demand. It is quite possible that, with the new emphasis put now on coal production, the supply beyond the year 1985 may exceed previous predictions. Thus, the availability prospects are good for alternative fuels derived from coal. Oil shale resources are not as plentiful as coal and domestic tar sands form substantially lower fossil fuel reserves than oil shale.

According to estimates of the National Petroleum Council and other sources, the domestic energy resource base for these fuels is $80,200 \times 10^{15}$ Btu (3.21×10^{12} tons) for coal, 9549×10^{15} Btu (1781×10^{9} bbl) for oil shale, and 127×10^{15} Btu (23.5×10^{9} bbl) for tar sands. For coal resources, $39,000 \times 10^{15}$ Btu are proven and $41,200 \times 10^{15}$ Btu are reasonably assured. For oil shale resources, 116×10^{15} Btu are proven, 1517×10^{15} Btu are reasonably assured, and 7916×10^{15} Btu are speculative. The tar sands figure is designated as a reasonably assured resource. Recoverable reserves are less than the figures cited and depend largely on extraction economics, extraction procedures, and possible legal restraints.

Nuclear energy, if developed at the rate forecast, could indirectly benefit the transportation sector by partially relieving the electric sector from the use of fossil fuels. These benefits to the electric sector could also be supplied by solar energy. This energy source will require a major technology breakthrough to be considered for use by the transportation sector. It cannot be considered for the near-term period (1975 to 1985) and may be problematical for use to the year 2000.

Based on all the aforementioned considerations, it would appear that synthetic gasoline and distillate hydrocarbons manufactured from coal and shale will offer the greatest promise for contributing to automotive fuel requirements in both the near-term and far-term periods. Coal-derived

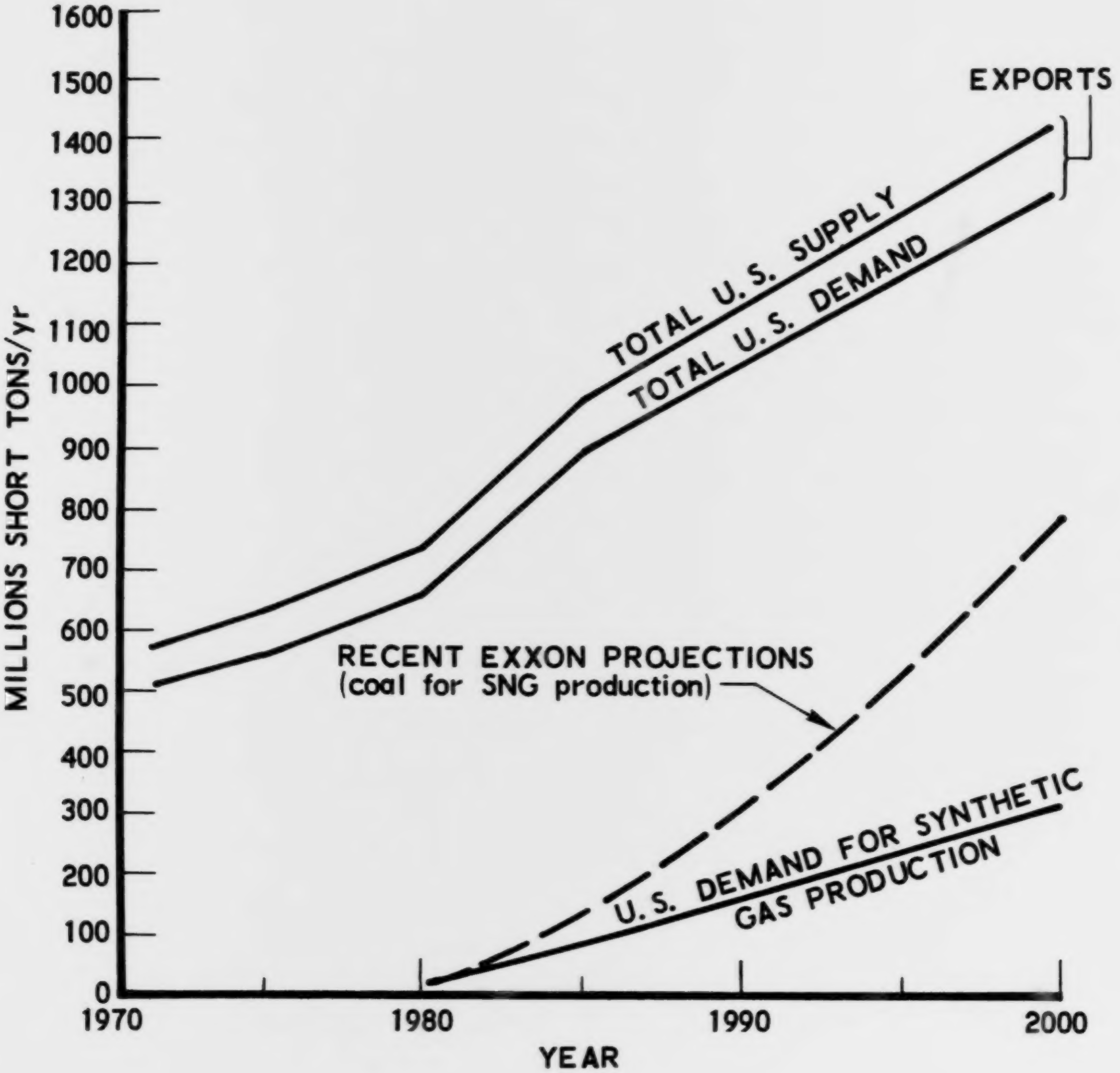

Figure S-1. Coal Demand/Supply Forecast* methanol, particularly in a methanol-gasoline blend, could be considered a secondary fuel source if certain technical problems can be solved. Another alternative fuel of merit is hydrogen, but it can only be considered as a significant contributor to automotive needs in the period beyond the year 2000. The rationale for these selections is amplified in the following discussion which presents a summary of the characteristics, attributes, and problem areas associated with each alternative fuel. Tabulated comparative data are also presented to summarize the overall alternative fuel picture in a more graphic manner.

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*Walter G. Dupree and James A. West, "United States Energy through the Year 2000," U.S. Department of the Interior, December 1970.

S. 2 STATUS SUMMARY OF ALTERNATIVE FUELS

S. 2. 1 Synthetic Gasoline and Distillate Hydrocarbon Fuels

Synthetic gasoline and distillate hydrocarbon fuels could be manufactured from coal, oil shale, tar sands, or organic solid waste products. They possess the primary advantage of expected complete compatibility with existing and advanced automotive power plants, as well as with distribution facilities down to the local gas station. Coal (particularly from strip mining processes) is by far the largest and most probable domestic energy resource available for synthetic fuel production, followed by oil shale. Tar sands and organic waste products show much less potential to meet projected energy needs.

The production cost in the post-1985 time period for gasoline and distillate hydrocarbon fuels derived from oil shale is estimated to be competitive with that for current costs of conventional petroleum-based sources. Equivalent liquid hydrocarbon fuels derived from coal are more expensive but are also competitive. The cost of petroleum-based fuels are determined by a combination of both foreign and domestic fuels costs; the foreign import costs are not within the control of this country.

The production economics for liquid hydrocarbon fuels derived from coal and shale will ultimately depend on (a) the efficient commercialization of various production processes currently under evaluation in laboratory and pilot-plant models, and (b) the transport distance required for raw and/or refined products. Intensive capital investment will be required if several 50,000 to 100,000-barrels-per-day plants are to be in operation in the 1980 to 1985 period.

Several processes are being investigated to make liquid hydrocarbon fuels from coal; one is in commercial production outside the United States, others are in the development stage or at a pilot plant scale within the United States. It is expected that the United States coal liquefaction industry will primarily be associated with western strip mine coal. This reflects the large resource base in this area, as well as low mining costs. Western coal has a further economic advantage because much of it has low sulfur content. The coal syncrude can be processed by extension of conventional refining technology.

The availability of shale oil for production of synthetic gasoline and distillate hydrocarbon fuels is very uncertain because of the difficulty in predicting production levels through the rest of the century. On the one hand, the resource base is extensive, the cost of production is moderate, and the technology is fairly well developed. On the other hand, there are very significant environmental problems. (As in the case for coal, waste product disposal constitutes a serious environmental problem, with contaminated water from oil shale processing being a critical concern.) Federal leases must also be made available, and the capital intensive mining and retorting must be carried out in remote locations. Costs of a specific shale oil recovery project are influenced by the richness of the shale, water availability, shale disposal facilities, general terrain, etc. Except for the construction of spur lines, it is expected that existing pipe lines can be used to transfer the syncrude from the first few plants, either to midwest or gulf area refineries. Projections indicate that shale oil cannot meet the total expected transportation fuel demand and that conventional petroleum or other synthetic fuels would be also needed.

The high cost of oil extraction from U. S. tar sands, combined with the limited resources, will most probably delay any major production of fuel from this source until the end of the far-term period.

The outlook for liquid fuel production from organic solid waste is highly speculative. Most development and pilot plant work will be confined to utilization of municipal waste, although design studies are being made of a plant to convert wood processing and logging wastes to oil.

Little information is available on the use of synthetic gasoline and distillate hydrocarbon fuels in automotive engines. A test program to investigate the compatibility of these coal- and shale-derived synthetic fuels with automotive engines is planned for Fiscal Year 1975 under an interagency agreement between EPA and the Bureau of Mines. In regard to the characteristics of these fuels, shale-derived transportation fuels will be probably almost indistinguishable from conventional petroleum fuel, while coal-derived fuels will have a much higher aromatic content. Emissions data are not yet available for synthetic hydrocarbon fuels in current or advanced automotive engines. A first step in obtaining such information will form part of the above-mentioned Bureau of Mines test program.

Major issues controlling the production levels of coal- and oil shale-derived synthetic fuels include the following: trends in petroleum refinery construction, expected automotive transportation fuel demands, and efficient and economic methods for processing coal and shale syncrude (both before 1990 when it will be a fairly small fraction of the total crude oil, and after 1990 when it could become a sizable fraction). The refined gasoline or distillate from both coal and shale will probably be blended with petroleum-derived analogs for quite some time.

S. 2. 2 Methanol and Methanol-Gasoline Blends

Industrially, methanol is used chiefly as a solvent and precursor in the manufacture of plastics, resins, and organo-chemicals. It also has been used as an automotive antifreeze, an automotive fuel in racing, and as a reciprocating aircraft engine fuel injectant.

Practically any organic matter, including fermentable matter, can be used to produce gases for the direct synthesis of methanol. The most economical domestic starting materials at present are hydrocarbons derived from natural gas or naphtha. Synthetic methanol production has climbed steadily in this country. Present production rates represent about one billion gallons annually, with new production capacity being achieved from larger plants. These larger units have also tended to improve economics.

Future production of methanol for transportation fuel will more likely come from solid fuels as starting materials for methanol synthesis. The primary constituent of the synthesis gas is hydrogen, along with carbon monoxide and, frequently, carbon dioxide. Coal is by far the largest and most probable domestic resource of this type available for methanol production. The technology in coal gasification is well founded, and funding is being accelerated to bring the various processes into the production stage. The practicality of converting oil shale to methanol is doubtful; it is more likely the derived liquids would be consumed directly as hydrocarbon fuels.

United States forest areas represent a potential source of organic raw material for methanol manufacture, since methanol is obtained as a byproduct in the destructive distillation of wood. The key economic question to be resolved is whether the insignificant cost of waste wood as raw material would sufficiently offset the large investment required in plant equipment and product distribution costs.

Methanol has many physical and chemical properties that are similar to gasoline. Aside from some operational problems, pure methanol has seen limited successful use with spark ignition engines powering automobiles. For this type of engine it offers the following advantages: (a) an increase in power from existing engines fueled with gasoline, largely because methanol heat of vaporization characteristics lead to increases in air inducted into the engine and to increases in net work output, and (b) an increase in efficiency and in power output per pound of engine weight for new engine designs, because the engine can operate at higher compression ratios than with high octane premium gasoline. It would also be generally compatible for use with future turbine engines, with relatively minor impact on such vehicles and their respective powerplants. Methanol is deemed suitable for use with other external combustion systems, for example, Rankine or Stirling engines, and some effort has been reported regarding fuel cell applicability. It is not suitable, however, for compression ignition (diesel-type) cycles because of its low cetane number.

Little data exist on emission levels for spark ignition gasoline engines run with pure methanol. The general trends seem to indicate, however, that emissions can be reduced for hydrocarbons, carbon monoxide, and oxides of nitrogen, although results were quite mixed and dependent upon the source of data and the conditions under which the engines were run.

Certain disadvantages of pure methanol will require that careful preparation by fuel distributors and automotive manufacturers precede its possible introduction into the retail sales market. Some of these disadvantages are discussed in the following paragraphs.

Fuel economy (in miles per gallon) with pure methanol is about half that with gasoline, necessitating a major increase in the size of the automobile fuel tank and modifications to the carburetor fuel jets [although the energy expended each mile (in British thermal units per mile) in powering an automobile with methanol is equivalent to the energy expended with gasoline].

Synthetic methanol distribution costs are expected to be higher than those estimated for synthetic gasoline because, for equal energy content, the pure methanol volume required to be piped, trucked, and stored is approximately twice that of gasoline. Therefore, when distribution costs are included, the cost at the pump to the consumer, per unit of fuel energy delivered (excluding tax), is estimated to be 10 to 30 percent greater than that for synthetic gasoline from coal and shale, respectively.

The boiling point of pure methanol is lower than that of the bulk of the constituents of gasoline, which may result in a greater incidence of vapor lock with current automobile fuel system designs. On the other hand, the vapor pressure of methanol is substantially less than that of the very lightest ends of gasoline. The latter being responsible for the good cold start properties of gasoline, manifold preheating would probably be required for cold starts with a carbureted methanol system.

Miscibility between pure methanol and water can result in the presence of water (from local atmospheric moisture) in the fuel distribution system, in the service station tanks, and in the vehicle tank, leading to possible corrosive action on metal surfaces in piping, tankage, and within the engine itself. Corrosion inhibitors may be required in the fuel to avoid this problem.

Because of the solvent action of pure methanol, paint, metal, and plastic surfaces may be damaged; solvent resistant materials must be considered for use in all applications.

Methanol-gasoline blends may offer a greater near-term advantage than pure methanol. This approach would conserve gasoline stocks to a small degree without necessitating major redesign of automobiles or engines. It should be noted, however, that even if methanol is added in a methanol-gasoline blend only to the five-percent level, current automotive fuel consumption would require about five times the present U.S. methanol production.

As with pure methanol, methanol-gasoline blends have a higher octane rating than gasoline alone. But there are indications that the motor octane number (MON) increase is not nearly as great as that which would be expected from measured increases in the research octane number (RON). This would indicate that engine road performance increases will not be as marked as those found in the laboratory.

Vapor lock and water miscibility problems would be present to a much greater degree with methanol-gasoline blends than with pure methanol. An example of these problems is the separation of gasoline and methanol in the presence of very small amounts of water, particularly at low temperatures. Solutions to these problems may be possible, but they require laboratory and road test verification.

The majority of published data on the application of methanol and methanol-gasoline blends to fueling automotive engines is about 20 to 30 years old. The use of new materials, engines, gasoline blends, and lubricating oils is a compelling factor for acquiring more contemporary characteristics of methanol in order to verify or invalidate older concepts regarding advantages and disadvantages of this alternative fuel. In this regard, the adaptability of methanol and methanol-gasoline blends to modern automotive systems will be explored systematically in a test program initiated by the Bureau of Mines through an interagency agreement with EPA. Other research programs investigating methanol and methanol blends are in progress or planned at several universities and industry research laboratories.

Methanol is known to be toxic, producing blindness through ingestion or narcosis through inhalation. There is a need for more information on extended low-level exposure to methanol such as would result from widespread use as a motor fuel.

In terms of fire safety, methanol fires should be easier to quench than gasoline fires because of its miscibility with water. On the other hand this miscibility will require special precautions to prevent fuel contamination, adulteration, and the corrosive effects previously discussed.

S.2.3 Methane (Natural Gas and Synthetic Natural Gas)*

Natural gas consists mostly of methane, with relatively small amounts of other hydrocarbons such as ethane, propane, butane, etc. Because of supply constraints of natural gas, efforts are under way to develop the technology for deriving synthetic natural gas from either coal or liquid hydrocarbons. A necessary constraint is that the synthetic gas be interchangeable with the natural gas as used by the power utility industry and the transportation industry.

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*Also referred to as Substitute Natural Gas

In the application of natural gas to the transportation industry, both compressed natural gas (at pressures up to 3000 pounds per square inch) and liquid natural gas are being used. Liquid natural gas is more attractive than the gaseous form because of its greatly increased density (resulting in reduced storage volume requirements on-board the vehicle) as compared with pressurized gas. However, the low boiling point requires application of cryogenic tank insulation techniques, which will add substantially to automobile tankage weight and cost relative to a conventional gasoline system. For example, liquefied natural gas fuel plus container will require an additional 100-pound weight and occupy approximately 2.2 times the volume of gasoline, including tankage provisions.

The production of synthetic natural gas from coal is particularly attractive. Production levels will depend on the completion of coal gasification plants expected to be in operation in the post-1980 period. It is expected that by 1985, 35 to 40 coal gasification plants, each producing approximately 250 million cubic feet per day, will be in operation, with a total output approaching nine billion cubic feet per day. The predicted supply of synthetic natural gas derived from coal in the year 2000 will be about 20 to 25 percent of the domestic production level of natural gas and may be expected to be of significance in replacing petroleum fuels for stationary electric generating plants.

Based on limited data, engine operation with methane is characterized by energy consumption, in British thermal units per mile, equal to or better than gasoline. There will be, however, a 10 to 15 percent drop in maximum power with gasoline-to-methane converted engines because of the greater volume occupied by gas than by semivaporized gasoline in the air.

The favorable characteristics of operation with natural gas or synthetic natural gas in a spark ignition engine are expected to apply to other alternative engines. These characteristics are ease of starting (particularly in cold weather), cleaner combustion with low emission of pollutants, and possibility of operation at lean air-fuel mixtures with high combustion efficiency.

Exhaust emissions from engines run on natural gas can be expected to be lower in general than those from gasoline-powered engines. A factor of importance is the reduced activity of hydrocarbon emissions with natural gas as opposed to the higher levels of activity with gasoline. (Total hydrocarbon activity is four to six times less with natural gas.) This should result in a reduction in photochemical smog. Data on exhaust emission levels and fuel economy for automotive engines powered by natural gas, synthetic natural gas, or liquid natural gas are quite sparse.

The toxicity of natural gas is indicated to be less than gasoline and it does not present a health problem. Natural gas may also be less hazardous than gasoline because its specific density is lower than air, which prevents formation of fuel-rich pockets near the ground in case of leakage.

However, the hazard of operation with natural gas and particularly liquid natural gas should not be underestimated. The low boiling point of LNG at atmospheric pressure will require overboard venting when the engine is not operative and the safe disposal of the boiloff by burning or dissipation in free air must be ensured. Information of a more extensive nature is required to evaluate the problem of boiloff of liquid natural gas from storage tanks.

As long as price regulation keeps natural gas prices low, current projections show the fuel cost per mile for natural gas as being lower than that for gasoline. The competitiveness of compressed natural gas or liquid natural gas with gasoline is, of course, highly dependent on fluctuations in price at the service station pump.

Considering the impact factors of economy of operation, safety, maintenance, fuel distribution, and refueling provisions, the use of natural gas will be limited mainly to fleet vehicle operation with depot refueling. Available gas supplies could also be used in stationary power plants, thus releasing some of the liquid petroleum for use by the automotive sector.

S. 2. 4 Propane and Butane

Liquid petroleum gas consists of various petroleum-associated chemical compounds whose boiling temperatures are below normal room temperature. The principal commercial products are propane and butane, and because of the chemical and physical properties of these compounds, they are the only potential liquid petroleum gas candidates considered here as alternative automotive fuels.

Crude oil wells, natural gas wells, light-hydrocarbon wells, and refinery operations are the principal sources of liquid petroleum gas (generally a by product in the production of natural gas and gasoline). Liquid petroleum gas domestic reserves are, therefore, related to the domestic crude oil and natural gas reserves. The primary production of liquid petroleum gas (approximately 74 percent of total production) comes from natural gas processing.

The use of liquid petroleum gas as an internal combustion engine fuel has a long history dating back to the early 1930s. The early commercial product was an uncertain mixture of propane, butane, and other gases with variable chemical and physical properties. Its use as an engine fuel resulted in many problems leading to disagreements as to its advantages and disadvantages. In 1962, the National Gas Processors Association adopted a specification for standardizing propane engine fuel and establishing the minimum level of propane and other standards of purity.

Propane appears suitable for use in all of the alternative engines currently being considered. In general, the use of gaseous fuels will provide for better mixing of the fuel-air charge, particularly in multicylinder engines where uniform distribution of the mixture from cylinder to cylinder and within each combustion chamber is difficult to achieve. This permits leaner mixtures to be used which may result in some measurable gain in specific fuel consumption. The ability of the engine to run on lean propane mixtures also tends to offer reductions in exhaust emissions of hydrocarbons, carbon monoxide, and oxides of nitrogen. Further, the reactivity of the exhaust products in reaction with sunlight (to form photochemical smog) is reduced when burning propane as compared with gasoline.

Based on test results for a converted 1969 327-cubic-inch-displacement Chevrolet engine operating at lean air-fuel settings ranging from 15 to 20, it appears that propane fuel offers a means of meeting the 1975 Federal interim emission standards. The emission control capability presently attainable through the use of propane fuel falls somewhat short of meeting the original 1976 Federal emission standards; vehicles tuned to achieve this capability show definite driveability problems associated with lean operation.

For the spark ignition engine, the high octane rating of propane permits a higher compression ratio to be used in the design, thereby improving the thermal efficiency and, accordingly, the specific fuel consumption characteristics of the engine. The overall improvement in fuel economy attainable through the use of propane in different engines is difficult to predict. For the conventional spark ignition engine, different users have experienced varying results depending upon the condition of the engine, weight of the vehicle, air-fuel mixture ratio, engine power setting, and a host of other variables.

Both propane and butane are relatively nontoxic gases and thus are safe to use.

Propane and butane can be stored in a liquefied state by either pressurizing the storage container or by cooling below relatively moderate boiling points. Of the two gases, propane is more generally suitable for on-the-road automotive vehicles because of its lower boiling point and higher octane rating. The lower boiling point of propane permits its use in colder climates where butane may require a separate heating source to vaporize the fuel for initial engine starting. Propane does, however, require higher tank storage pressures than butane to maintain it in a liquid state.

Because the current major production source of propane and butane is natural-gas processing plants, a new raw material source and production process for obtaining liquid petroleum gas would be required to increase its availability. Economically acceptable methods of producing liquid petroleum gas directly from coal or from oil shale are needed. But even if costs of production of liquid petroleum gas from coal by either gasification or liquefaction are reduced, the production of gasoline from coal would be more efficient in terms of energy utilization. Considering this factor as well as the problems in establishing a nationwide distribution and storage system, this fuel is not considered a primary candidate for large-scale automotive use. Rather, it may find application to commercial fleet operations.

S. 2. 5 Ethanol

Ethanol or ethyl alcohol has been produced over the centuries by fermentation of various carbohydrates (sugars) and is now mainly manufactured synthetically for industrial use from petroleum-derived ethylene. The principal industrial uses of ethanol are (a) as a chemical intermediate, (b) as a solvent, (c) as an antifreeze, and (d) in fine chemical manufactures such as drugs, polishes, perfumes, and cosmetics. It is mainly known by virtue of its use in alcoholic beverages as the principal product of fermentation. Most of the ethyl alcohol production outside the United States is accomplished by the fermentation process. Fermentation alcohol production is affected by very complex cost economics involving domestic availability and stability in the price of ethylene versus the widely fluctuating availability of agricultural raw materials around the world.

Ethanol has been demonstrated to be compatible as a motor fuel with present vehicles. In many parts of the world, it has been blended in concentrations varying between 10 and 20 percent to alleviate gasoline shortages. Like methanol, it has not proved to be economical for such use in the United States because it has a lower calorific value per unit weight or volume than gasoline while being more costly than domestic gasoline.

Studies over the years have demonstrated that the use of alcohol as an automotive fuel reduces fuel mileage essentially in proportion to the reduction in lower heating values of the fuels. For pure ethanol, this corresponds approximately to a 60 percent increase in fuel consumption. Experiments with single-cylinder engines and multicylinder-engine-powered vehicles generally have tended to verify this; however, comparison of relative fuel consumption levels is influenced to some degree by the type of engine used and the duty cycle. The most favorable test data for ethanol-gasoline blends indicate fuel economy about equal to that of gasoline on a Btu per mile basis.

While some data are available concerning the exhaust pollution effects of ethanol, the literature is far from comprehensive. Some recent efforts have dealt with ethanol-gasoline blends of approximately 25 percent by volume. The results in single-cylinder test engines compared on the basis of equivalence ratios* show that the emissions are controlled by the primary fuel constituent (gasoline) in the blend and are essentially the same as for gasoline alone.

The rationale of using ethanol as an antiknock replacement for tetraethyl lead is not convincing, since there are other compounds, for example, methanol, that are cheaper and at least as efficient; pure ethanol or blends with gasoline have essentially the same usage problems cited for methanol.

Ethanol is not highly toxic. If inhaled for continuous periods under poor ventilation conditions, discomfort occurs such as coughing, eye irritation, headache, and related symptoms.

Although ethanol is being produced in large quantities, projected availability is not expected to improve in the near term to the level required to support its use as a motor fuel. The economics of ethanol production and poor fuel economy are major factors tending to limit its use. New methods are needed to enable low-cost synthesis of ethanol on a very large production scale. Otherwise, it will not be competitive with other prospective automotive fuels.

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* $$\frac{(\text{fuel-air ratio})_{\text{actual}}}{(\text{fuel-air ratio})_{\text{stoichiometric}}}$$

S. 2. 6 Hydrogen

The United States space program has created a large demand for hydrogen as a primary rocket engine fuel for combustion principally with oxygen, but its main use in this country is in the production of ammonia. Hydrogen can be produced from all fossil hydrocarbons including natural gas, oil refinery gas, liquid petroleum, natural gasoline, naphtha, fuel oil, crude oil, coal, and coke. Hydrogen is currently produced primarily from hydrocarbons, using steam reforming or partial oxidation processes. It is also produced commercially from water electrolysis. Although the supply of hydrogen from water is virtually inexhaustible, facilities for mass production are not yet available and will be dependent on a greater availability of nuclear power sources.

Under combustion with oxygen in an automotive power plant, hydrogen offers the complete elimination of hydrocarbons, carbon monoxide, and oxides of nitrogen. However, oxygen would have to be stored on-board the vehicle. By contrast, with air combustion oxides of nitrogen, emissions are expected. The level of emission is highly dependent on the combustion temperature because oxides of nitrogen emissions increase with increases in temperature. Low combustion temperatures (and lower oxide of nitrogen emissions) are achievable by using lean fuel mixtures.

Experimental work using modified gasoline engines fueled with hydrogen-air mixtures have shown good fuel economy. On a Btu per pound basis, hydrogen-fueled cars can have a comparable fuel economy to cars operating on conventional fuels. There is, however, a concomitant loss of maximum power.

In regard to toxicity effects, gaseous hydrogen acts as a simple asphyxiant.

Because its flammability limits when mixed with air are very wide and its ignition energy is very small, a hydrogen fire is easier to create than a gasoline fire. An unconfined mixture of hydrogen and air will burn but not detonate if it is exposed to a limited ignition source such as a spark. Explosion can occur in confined areas or when ignition is accomplished by a shock source equivalent to a blasting cap or a small explosive charge. The required safety precautions for handling hydrogen are, therefore, more stringent than those required for conventional fuels.

Furthermore, because the storage temperature of liquid hydrogen is below -423°F, there are significant and unique hazards. This temperature is low enough to liquefy all other gases except helium. Any part of the hydrogen tank or transfer line that becomes cooled to this temperature level and is exposed to air will liquefy the air. Because of the difference in boiling points between oxygen and hydrogen, the resulting liquid will become enriched in oxygen buildup with a consequent dangerous fire hazard.

Although hydrogen appears to be highly suitable as a fuel for automobiles, a major technical drawback is the problem of on-board storage. Four methods of storage on-board a transportation vehicle can be considered: (a) as a pressurized gas at ambient temperature, (b) as a cryogenic liquid at -423°F, (c) as a metal hydride, and (d) in a chemical compound such as ammonia. As a compressed gas, 40 standard cylinders would be required to provide reasonable driving range. Clearly, compressed gas is not feasible even with lightweight cylinders. In liquid form, the tank capacity required is more than three and one-half times that required for gasoline on an equivalent energy (British thermal unit) basis. In addition, the method of tank insulation and fabrication is complex and could prove to be expensive. In the case of a metal hydride, it can be decomposed on the vehicle by the addition of heat to provide hydrogen and it can be replenished at filling stations supplying hydrogen gas. Research work is under way to develop this process and reduce the excess system weight, but it is too early to assess ultimate feasibility at this time. (Storage as ammonia is discussed in the next section).

On an equivalent energy basis, liquid hydrogen cost to the consumer is estimated to be much greater than the cost of gasoline or distillate from coal. Much of this cost is attributable to significant cost items connected with the liquefaction of hydrogen and its subsequent transportation to, and storage at, retail outlets. Hence, a major obstacle to using hydrogen as a universal fuel is one of economics. Extensive and long-range programs may possibly lead to a narrowing of the gap between the cost of hydrogen and the cost of fossil fuel.

Furthermore, capital investment requirements are quite large. Recent estimates of capital costs for large-size production plants (2500 ton-per-day capacity) indicated a coal conversion plant cost of $1.2 billion and a nuclear-powered water electrolysis plant cost of $2.7 billion. The lower value is approximately 60 percent higher than plant investment for coal-produced gasoline (on equal British thermal units per day basis).

Technically, it is not difficult to make hydrogen from coal, but it is an inefficient means of using coal energy. A more practical, though more costly, means of producing hydrogen is by application of nuclear energy to dissociate water. Unfortunately, delays in current implementation of this form of energy have led to predictions of reduced future availability. Using optimistic assumptions regarding this availability for production of hydrogen fuel, it is estimated that no more than a small percentage (about 9%) of automotive fuel demands could be met even by the year 2000. Even if nuclear energy could somehow be made available to a greater degree at earlier dates, the massive capital requirements for hydrogen manufacturing plants and distribution facilities, and the extensive period needed for actual construction activities, preclude any earlier consideration of this fuel as a major contributor to passenger car needs.

A greater benefit may be derived from application of nuclear energy and nuclear-derived hydrogen to (a) release of petroleum fuels from power-generating stations (thereby making them available for automotive use) and (b) providing hydrogen for coal conversion processes such as in the manufacture of synthetic gasoline and distillate hydrocarbon fuels.

S. 2. 7 Ammonia

The interest in ammonia as an engine fuel stems from the consideration that it allows the storage of hydrogen in nitrogen hydride form at a relatively low pressure (250 psig) when at ambient temperature, without some of the fire and explosion hazards associated with pure hydrogen. Additionally, the products of combustion will contain neither carbon monoxide nor unburned hydrocarbons; oxides of nitrogen, however, will be present.

Basically, ammonia is produced by catalytic synthesis from hydrogen and nitrogen. Practically all current production of ammonia is from natural gas or petroleum-derivative sources. The nonpetroleum or natural gas derivative chemical feed stocks considered most suitable for ammonia process manufacture via the hydrogen route are coal and oil shale. Other methods, such as water electrolysis, can also be used to produce hydrogen.

The net heating value of ammonia is 8000 British thermal units per pound, compared with a heating value of 19,000 British thermal units per pound for gasoline. This indicates that for equal combustion efficiencies and for equal energy outputs, the weight of ammonia required will be 2.4 times the weight of gasoline. Based on this figure, the volume of ammonia would be about 2.8 times that for gasoline. Because it requires approximately this much more ammonia by volume on the average to drive equivalent miles using conventional engines, the consumer costs of ammonia would be several times that of current gasoline.

The possibility of the presence of unburned ammonia in exhaust emissions raises the concern that these ammonia gases may be discharged directly to the atmosphere and prove harmful to health. The physiological effects of ammonia are directly traceable to its ability to produce local severe irritation of tissues. It is extremely irritating and highly corrosive to the eyes and respiratory tract. Suffocation and death from pulmonary edema can result from exposure to high concentrations. Hence, the fuel transfer system in the vehicle will have to be a closed and pressurized system.

To produce sufficient ammonia for complete replacement of gasoline as an automotive fuel, and if ammonia were produced by conventional processes from naphtha or natural gas, industry would have to make a capital investment of approximately $54 billion. However, because naphtha and natural gas are in short supply, ammonia will more likely have to be made by coal gasification or water electrolysis. The capital costs for producing ammonia from coal would exceed the $54 billion for ammonia produced from naphtha, because of the additional capital required for coal gasification plants. Likewise, if ammonia were produced by water electrolysis, investment costs would be even greater. In view of the many other problems associated with ammonia usage, it does not appear to be a promising alternative fuel.

S. 2. 8 Hydrazine

Hydrazine derivatives are used today in the plastic industry, in the pharmaceutical industry, and predominantly as fuel for rocket propulsion. Hydrazine has heretofore not been considered as an automotive fuel, although it could find application in fuel cells for electric vehicles.

The hazards to health and safety may be an inhibiting factor to the use of hydrazine as an automobile fuel. Anhydrous or aqueous solutions of hydrazine are toxic by ingestion, inhalation of vapors, or contact with the skin. Also, because mild steel is incompatible with hydrazine due to the presence of oxides, stainless steel must be used for fuel containers and for transfer piping.

Anhydrous hydrazine is now being delivered to the U. S. Air Force under contract at a cost of $1.23 per pound. It is anticipated that the cost of hydrazine may be lowered to $0.75 per pound in large tonnage production. These costs are an order of magnitude higher than those for gasoline-powered automobiles, when compared on a utilization-per-mile basis.

Capital costs for hydrazine production facilities would be certainly higher than costs for hydrogen or ammonia plants because these liquids are mainly feedstocks for the formulation of hydrazine. The many deficiencies of hydrazine as a potential automotive fuel lead to the conclusion that it is unsuitable as an alternative to petroleum-based fuels.

S. 2. 9 Fuels Reformed On-board the Vehicles

Operation of a spark ignition internal combustion engine at lean air-fuel ratios (greater than 15 to 1) can result in the reduction of exhaust emissions without the addition of emission control devices. Currently, gasoline engines are normally operated at air fuel ratios below approximately 17 to avoid rough engine operation.

One approach that is being investigated as a means of extending the lean operating limits of gasoline engines in order to achieve low exhaust emissions is the incorporation of a fuel reformer device between the gasoline tank and the carburetor of the gasoline engine-powered conventional automobile. The fuel reformer device converts all or a portion of the engine's fuel requirements from gasoline (or other liquid hydrocarbon fuel) to a gaseous combustible product (principally hydrogen) prior to induction into the engine. It should be noted that such lean operation causes reduced engine power that would necessitate the use of a larger displacement engine for the same maximum power output.

In general, reformed fuels may be processed from a variety of liquid hydrocarbon fuels including: gasoline, kerosene, jet fuel, diesel fuel, home heating oil, heptane, hexane, and liquid petroleum gas. Specific reformer devices or systems, however, may be designed to operate on a single grade of hydrocarbon fuel or a more limited range of hydrocarbon fuel choices. Thus, reformed fuels are in turn limited by the reserves and/or raw material sources for conventional petroleum or nonpetroleum hydrocarbon liquids.

Improved fuel economy for vehicles operated with reformed fuels has been postulated to result from (a) higher engine thermal efficiencies as a result of lean operation, and (b) reduced throttling losses at part-load conditions by using fuel throttling control instead of air or intake charge throttling; this latter approach is rendered feasible because of the combustibility of hydrogen-air mixtures over the wide range of air-fuel ratios that would be encountered during unthrottled part-load engine operation.

Engine-indicated thermal efficiencies were measured by General Motors for a single-cylinder engine operating on hydrogen-supplemented gasoline. The indicated thermal efficiency increased from 33 percent to about 37 percent. Similar trends were observed by the Jet Propulsion Laboratory in tests of a single-cylinder CFR engine and a 350 cubic-inch-displacement V-8 engine. But substantive fuel economy data from vehicle tests are currently not available.

A prototype model of the International Materials Corporation reformer was tested in simulated vehicle operation. This system, which converts all of the engines fuel requirements, demonstrated exhaust emissions in grams per mile of 0.412 to 2.78 for CO, 0.012 to 0.15 for HC, and 0.040 to 0.37 for NO_x. However, reformers of this type (i.e., reform all of the engine fuel requirements) are typically large in volume and pose difficult vehicle packaging problems. In addition, reformer inefficiencies are applied to all of the gasoline used by the vehicle and may result in reduced fuel economy.

The Jet Propulsion Laboratory recently conducted comparison tests of a 1973 Chevrolet Impala on the 1975 Federal Test Procedure. The first set of tests were run with gasoline only and the second set of tests were run with hydrogen-supplemented gasoline to partially simulate expected supply of hydrogen that would eventually be provided by an on-board reformer converting a portion of the engines fuel requirements. (The reformer has been undergoing development in laboratory tests.) The hydrogen was supplied from hydrogen gas bottles located in the trunk of the car. The reduction in CO and NO_x emissions was marked, but HC emissions were high.

Similar to the Jet Propulsion Laboratory test configuration, in-the-engine control of NO_x was also verified by General Motors in one experimental vehicle with hydrogen-supplemented gasoline; the hydrogen was supplied by gas bottles in the trunk of the car. These exhaust emissions tests were conducted on the cold start 1975 Federal Test Procedure at 3500 pounds inertia weight. NO_x and CO emissions satisfied the 0.4 and 3.4 gram-per-mile original 1976 Federal standards, respectively. However, the HC emission was nearly an order of magnitude higher than the 0.41 gram-per-mile limit.

All the foregoing tests were exploratory and they may not reflect the ultimate system potential for engines operated on reformed fuel, nor the case of gasoline supplemented by either hydrogen or reformed fuel.

All the liquid hydrocarbon fuels which are potential candidates for use with fuel reformers are in commercial use today, with contemporary handling, storage, and distribution systems. This fact enhances the potential for use of reformed fuel systems since no new handling, storage, or distribution systems would be required.

Fuel reformer concepts are still in the exploratory, proof-of-principle, or feasibility determination stage. A number of critical data gaps must be filled before the potential of reformed fuels can be fully assessed. NASA has been funding the Jet Propulsion Laboratory to acquire data and prove concept feasibility, and EPA is providing supplemental funding for this work in addition to other contractor-supported programs for evaluation of similar concepts.

S.3 COMPARATIVE REVIEW OF ALTERNATIVE FUELS

The foregoing summary of each alternative fuel is now presented on a relative basis in succeeding paragraphs.

A comparison of physical characteristics for the alternative fuels being considered is given in Table S-1. The various processes associated with manufacture of these fuels are summarized in Table S-2 and are discussed briefly below.

The production of synthetic gasoline and distillate hydrocarbon fuels obtained from coal or oil shale is now in the pilot plant stage of process development and it would probably be close to 1985 before any appreciable quantities could be made available to the transportation sector. By then, approximately 3-billion gallons per year of liquid petroleum from coal and 14-billion gallons per year from oil shale can be made available. Production rate will be paced by available investment funds and the mining rates for coal and oil shale.

The manufacturing processes for methanol and ethanol from petroleum are well established, but, in the derivation from coal of synthetic gas and ethylene, the production processes require further development. Considering this fact, the availability of these fuels for the transportation sector would be similar to that of synthetic gasoline and they could be a viable contributor to energy needs in the far-term period (1985-2000).

Methane in the form of compressed natural gas or liquid natural gas processed from coal is in the development stage, but significant quantities will not be available before 1985 (1.1 trillion cubic feet per year equivalent in Btu to 10-billion gallons of gasoline). Thereafter, availability is projected to approximately 8.5 trillion cubic feet per year in the year 2000.

With regard to propane and butane, the discussions pertaining to methanol and ethanol would apply in this case.

Hydrogen gas is produced either by partial oxidation of hydrocarbons or electrolysis of water. Other processes are under development.

Table S-1. Comparative Physical Characteristics of Alternative Nonpetroleum-Based Automotive Fuels[a, b]

Fuel	Heat of Combustion (Lower) Btu/lb	Heat of Vaporization at Normal Boiling Point Btu/lb	Normal Boiling Point °F	Vapor Pressure at 100°F Psia	Density		Freezing Point °F
					Liquid lb/ft³	Gas, STP lb/ft³	
Gasoline	18,650	150	100 - 400	8 - 12	46.0	NA	<-40
Distillate (Includes naphtha through fuel oil)	18,400	110	375 - 620	0.01	52.6	NA	-40 to +5
Methanol (CH_3OH)	8,640	474	149	4.6	49.7	NA	-142
Ethanol (C_2H_5OH)	11,550	360	173	2.4	49.3	NA	-179
Methane (CH_4)	21.500	219	-259	Above crit. temp.	27.9	0.045	-296
Propane (C_3H_8)	19,940	183	-48.1	189	31.8	0.1196	-309.8
Hydrogen (H_2)	51,600	194	-423	Above crit. temp.	4.43	0.0056	-435
Ammonia (NH_3)	8,000	591	-28	212	38.0 (70°F)	0.0433	-108
Hydrazine (N_2H_4)	7,290	540	236	0.57	62.4	NA	35.6

[a] D. P. Gregory and R. B. Rosenberg, "Synthetic Fuels for Transportation and National Energy Needs", SAE Paper No. 730520 (1973)

[b] Hydrogen and Synthetic Fuels, Atomic Energy Commission, Report No. UC-80(September 1972)

Table S-2. Production Processes for Alternative Nonpetroleum-Based Automotive Fuels

Fuel	Process Alternatives	Development Status	Technology Needs
Gasoline/Distillate	1. Coal liquefaction 2. Coal gasification→synthesis gas gasoline via Fischer-Tropsch process 3. Oil-shale extraction	1. Pilot plant 2. Commercial production in South Africa. Inefficient, costly. 3. Ready for commercial plant	1. Catalyst, material handling, hardware development 2. Make more selective, handle caking coals 3. Disposal of spent shale and water; deep mining techniques
Methanol	Coal gasification→synthesis gas (carbon monoxide and hydrogen) in presence of catalyst	Commercial production demonstrated	Gasification process improvement
Ethanol	Fermentation of agricultural products (sugar, starch, cellulose)	Commercial production	Present fermentation technology too expensive. Need new rapid fermentation process.
Methane	Coal gasification→synthesis gas (carbon monoxide plus hydrogen)→catalytic methanation	Commercial production with methanation step now being demonstrated.	Gasification process improvement.
Propane	By-product in coal gasification or liquefaction	Same as coal liquefaction and/or gasification	Develop efficient byproduct extraction from coal processing
Hydrogen	1. Water electrolysis 2. Coal gasification→synthesis gas (carbon monoxide plus hydrogen)→shift converter→carbon dioxide scrubber 3. Thermochemical	1. Commercial production 2. Pilot plant 3. Laboratory	1. Improve cell efficiency 2. Efficient carbon dioxide removal, gasification process improvements 3. Simple, energy-efficient chemical steps. Avoid corrosive, unstable materials
Ammonia	Hydrogen plus nitrogen in presence of catalyst	Commercial production with H_2 from natural gas	Same as for hydrogen above
Hydrazine	1. Raschig process 2. Urea process	1. Commercial production 2. Commercial production	New, cheaper process required. Thermodynamics limit possible savings.

Data are primarily from F. H. Kant, et al., Feasibility Study of Alternative Fuels for Automotive Transportation (in three volumes), EPA-460/3-74-009-4-a, Exxon Research and Engineering Company (June 1974).

A ton of coal can yield only a certain amount of liquid petroleum products and a certain amount of hydrocarbon gases with residual char and by-products. Any amount of hydrogen shiphoned off this process will reduce the amount of either liquid petroleum or gas produced. With that understanding, the availability of hydrogen is also regulated by the coal processing rate and the demand for alternative synthetic fuels. Hydrogen availability could increase in the far term period when breeder reactors could be used for the production of electricity needed for the water electrolysis process. But production rates are not likely to be significant to the transportation sector before the year 2000.

Ammonia and hydrazine processes are defined, and the comments regarding future availability are similar to those for hydrogen.

A variety of parameters determining the suitability of alternative fuels for automotive application are summarized in Table S-3. A summary of the highlights for each fuel considered is presented in Table S-4. The succeeding discussion elaborates on the information given in these tables.

From the fuel costs at the pump (excluding tax) given in Table S-3, it can be seen that synthetic gasoline and distillate hydrocarbons manufactured from shale are potentially the least expensive alternative fuels. These same synthetic fuels made from coal are also favòrable from an economic standpoint, particularly if petroleum product prices continue to rise. Next in order for favorable consideration would be methanol. (Methanol-gasoline blends would be even more attractive price-wise.) Fuels such as hydrogen, ethanol, ammonia, and hydrazine are poor economic contenders.

The costs shown in Table S-3 are for the post 1985 period but are given in 1973 dollars. These estimates, of course, are highly dependent on a host of complex interacting factors such as: (a) environmental control during mining or conversion processes, (b) manufacturing scale of operations, (c) rate of progress in improving process efficiencies, (d) the type of manufacturing process, (e) capital investment requirements and allowable rate of equipment depreciation, (f) logistics of distribution and storage. Costs for

Table S-3. Logistic Factors for Use of Alternative Nonpetroleum-Based Automotive Fuels

Fuel	Est. Cost at Pump in 1973 Dollars (Taxes Excluded) $/$10^6$ Btu[a]	Vehicle Storage	Toxicity	Safety	Compatability with Petroleum Fuels	Status of Distribution to Consumer
Gasoline[b]	3.15 (from coal) 2.60 (from shale)	Excellent	Medium	High fire hazard	--	Existing
Distillate[b]	2.50 (from coal) 2.00 (from shale)	Excellent	Low	Low fire hazard	High	Existing
Liquid Hydrogen	7.00 (from nuclear electrolysis) 4.70 (from coal)	Poor	Low	High fire and explosion hazard	Low	Major development and investment required
Ammonia	7.65 (using hydrogen from electrolysis)	Fair	High	Moderate fire hazard	Low	Some experience in farm distribution. Major expansion required with emphasis on safety
Hydrazine	Over 20	Good	High	High fire and explosion hazard	Low	Major modifications to existing gasoline system in areas of materials compatibility and safety
Methanol	3.40 (from coal)	Good	Medium	Moderate fire hazard	High if water contamination controlled	Existing gasoline system could be used with modifications to prevent water contamination and corrosion
Ethanol	7.80 (from organic waste)	Good	Low	Moderate fire hazard	High if water contamination controlled	Same as Methanol
Methane	3.80	Poor	Low	High fire and explosion hazard	Low	About the same problem as for Hydrogen
Propane	Greater than 3.80 (from coal liquefaction)	Fair	Low	Moderate fire hazard	Low	Limited availability at present. Requires extension

[a] $/$10^6$ Btu = Dollars per million British thermal units for the post-1985 period. Data are primarily from F. H. Kant, et al., Feasibility Study of Alternative Fuels for Automotive Transportation (in three volumes), EPA-460/3-74-009-4-a, Exxon Research and Engineering Company (June 1974).

[b] Currently at the pump, gasoline from petroleum at 38¢ per gallon is equivalent to $3.35/$10^6$ Btu and distillate from petroleum at 37¢ per gallon is equivalent to $2.80/$10^6$ Btu (taxes excluded).

Table S-4. Summary of Availability and Suitability of Alternative Nonpetroleum-Based Automotive Fuels

Fuels	Present Energy Source	Future Energy Source	Fuel Available in Limited Quantity (Near-Term Energy Source)	Fuel Available in Significant Quantity (Future Energy Source)	Future Suitability for Automotive Use	Research Gaps in Engine Application	Factors Inhibiting Fuel Use
Synthetic gasoline and distillate hydrocarbon	Liquid petroleum	Coal, oil shale	Pre-1985	Post-1985	Excellent	More engine data	Major factors identified
Methanol,[a] Ethanol	Natural gas, liquid hydrocarbons	Coal, possibly solid waste	Pre-1985	Post-1985	Good, Fair	More engine data	Cost, performance, compatability factors
Methane (CNG or LNG)	Natural gas	Coal, possibly solid waste	Pre-1985	Post-1985	Fair	More engine data. Resolve storability problem	On-board storage, distribution network
Propane, Butane (LPG)	Natural gas, liquid hydrocarbons	Coal	Pre-1985	Post-1985	Fair	More engine data	More expensive than synthetic gasoline and similar fuels
Hydrogen	Petroleum, gas, coal, water (by electrolysis)	Coal, nuclear (electrolysis)	Post-1985	Post-2000	Fair to poor	More engine data. Resolve storability problem	On-board storage, distribution network, safety
Ammonia, Hydrazine	Same as hydrogen	Same as hydrogen	Post-1985	Post-2000	Poor	Not worth pursuing	Toxicity, safety, cost
Reformed fuels	Liquid hydrocarbons	Coal, oil shale	Post-1985	Post-1985	Fair	More engine data. Development of fuel reforming	Cost and complexity

[a] Possible application when mixed with gasoline (methanol blend).

CNG = compressed natural gas
LNG = liquid natural gas
LPG = liquid petroleum gas

later periods are expected to decline as process refinements and operational experience are applied to new, and larger, facilities. On the other hand, fuel costs may increase due to the increased cost of extracting raw materials from the ground.

An estimate of the possible production implementation for several alternative fuels is presented in Table S-4 for both near-term and far-term periods. As can be seen, gasoline and distillate hydrocarbon fuels derived synthetically from coal or shale rank highest in terms of probable implementation and timeliness in response to meeting current fuel shortages; this is particularly true of shale-derived fuels. The primary reasons for this ranking are (a) similarity of these fuels to current products in use, (b) the ready availability and extensive domestic reserves of coal and shale, and (c) a recognized acceptable technology for converting coal and shale to syncrude.

Methanol has been run satisfactorily in spark ignition engines. Its low heating value (in Btu per pound), as compared to gasoline, results in over twice the fuel consumption when expressed in miles per gallon. However, the cost per Btu is approximately equal to that of gasoline. From a desirability standpoint, it should be noted that the emissions of NO_x with methanol are lower than those with gasoline. Mixes of methanol with gasoline can also be considered. However, there are two major factors which mitigate against methanol-gasoline blends at present: water absorption susceptibility (leading to phase separation and corrosion of containers) and high volatility (leading to vapor lock).

Ethanol has shown performance similar to gasoline in the spark ignition engine but its cost is higher than that of methanol. Consequently, its future application to automotive engines is doubtful.

Methane, when used in automotive engines, gives performance equal to or better than gasoline with a reduction in all primary exhaust emissions. But the problem of storage on board the vehicle and the need for a distribution network are factors inhibiting its use.

Propane and butane (liquified petroleum gas) have been used successfully in automotive engines and some reductions in exhaust emissions were noted. The lower heating values of liquified petroleum gas and the lower density result in higher fuel consumption reflected in reduced miles per gallon when compared to gasoline. However, on an equivalent energy basis, it is more expensive than gasoline. Distribution of liquified petroleum gas is at present limited and storage on-board the vehicle is more complicated than that of gasoline, requiring pressurized tanks to keep the fuel in liquid phase.

Hydrogen fuel can burn with air in an automotive engine at very lean air-fuel ratios with fuel economy comparable to that of gasoline (when expressed in miles/Btu). Exhaust emissions are low and theoretically there should be no carbon monoxide or hydrocarbons present (except that produced in burning of lubricating oil); oxides of nitrogen levels are substantially lower than those for gasoline engines. Costs are quite high when compared with other fuels, and a means of safe, efficient distribution to the consumer is a major problem to be resolved. Another problem is that hydrogen density is low even in the cryogenic phase (1/12 that of gasoline) and this creates a problem in storability (large volume containment) aboard the vehicle. This problem might be alleviated by the use of solid metal hydrides that are under development by the Federal government and commercial interests, but weight reduction is needed for assurance of a practical system.

Compared to gasoline ammonia has a low heating value (fuel consumption is over twice that obtained with gasoline) and NO_x emissions are higher. Storage of ammonia on-board the vehicle requires pressurized tanks. Production costs are much higher than synthetic gasoline and distillate fuels.

Like ammonia, hydrazine has a low heating value. No data are available for its use with automotive engines. This fuel is not considered as a serious contender for automotive application because of high cost, toxicity, and potential explosive hazard during transportation. An alternative use of hydrazine in the far-term period could be for fuel cells. But costs are prohibitively high when compared with other alternative fuels.

Fuels reformed on-board the vehicle are generated by thermal decomposition of hydrocarbons and consist primarily of hydrogen and carbon monoxide. Such gas generator systems are now under development to permit engine operation at lean air-fuel ratios with anticipated improvements in fuel economy and exhaust emissions compared to operation with gasoline.

Of importance is the adaptability of various types of fuels to the personal passenger car in a form which can find wide public acceptance. One criterion for ranking fuels is the relative weight and/or volume required for storage in the vehicle. To retain acceptable vehicle seating arrangements and safe handling characteristics, practical fuel storage designs should come reasonably close to the type of packaging that has evolved through use of the current petroleum-derived fuels. A comparison of the tankage requirements for several fuels is presented in Table S-5. Some fuels come reasonably close to the weight and volume for gasoline, but nonetheless are still overweight and oversize by factors of 2 to 3.

Research needs for alternative fuels constitute (a) refinement of processes for the manufacture of automotive fuels from coal and shale, (b) further evaluation of on-board vehicle reformed fuel processes, (c) evaluation of the most promising alternative fuels for various alternative engines, and (d) defining the safety, handling, and storage regulations of those fuels with physical characteristics markedly different from gasoline.

The choice of a given fuel for automotive use will be, in part, a function of alternative fuel availability discussed before. It will also depend on the time and funding allocated to close the general research gaps enumerated above, and to resolve the specific problems connected with application of these fuels to automotive power plants.

Table S-5. Comparison of Tankage Requirements for Alternative Nonpetroleum-Based Automotive Fuels

Basis: Energy Equivalent of 20 gallons of gasoline[a] (2.27×10^6 British thermal units)

Fuel	Fuel Alone		Fuel and Container	
	Weight, lb	Volume, ft^3	Weight, lb	Volume, ft^3
Gasoline[b]	119	2.59	134	2.76
No. 2 Diesel fuel[c]	120	2.28	134	2.50
Hydrogen (gas) at 3000 psi, 80°F	43.9	40.6	1330	89.2
Hydrogen (liquid) at one atmosphere	43.9	10.18	392	15.2
Hydrogen as magnesium hydride[d]	577	6.6	750	9[e]
Methane (gas) at 3000 psi, 80°F	105.5	12.40	500	14.6
Methane (liquid) at one atmosphere	105.5	4.06	240	6.1
Ammonia (liquid) at 80°F	284	7.16	455	7.5
Hydrazine	338	5.40	367	6.05
Methanol	261	5.26	285	5.70
Ethanol	195	3.95	214	4.78
Propane (liquid) at 250 psi	106	3.34	220	4.6

[a] On an equal mileage basis (say 270 miles) the fuel storage requirements must be adjusted for the thermal efficiency of the vehicle. In the case of diesel power the above figures would be reduced by one-third.

[b] This assumed to apply to all gasoline whether from petroleum, coal, or shale.

[c] This assumed to apply to all distillate fuels whether from petroleum, coal, or shale.

[d] Assumes theoretical yield of hydrogen, density of magnesium hydride is 1.4 grams per milliliter.

[e] Does not include means for heat exchange and ancillary equipment to charge and discharge magnesium hydride.

lb = pounds ft^3 = cubic feet   psi = pounds per square inch

SECTION 1

INTRODUCTION

The objective of this volume of the report is to review the current status of alternative (to petroleum-based gasoline) fuels for use in automotive engines. The need for such a review received additional emphasis from a series of well-publicized events occurring near the end of calendar year 1973. These events brought sharply into focus the worldwide fossil fuel shortage and the curtailment in U.S. imports of petroleum products.

Of necessity, this report utilizes predictions in energy demand (consumption) and supply growth which are based on a previously observed and extrapolated trend. Such predictions are illustrated in Figure 1-1, which shows an almost constant rate of growth in U.S. energy consumption until the year 2000. It was based on a 1 percent per year population growth and an annual GNP growth of 4.3 percent until 1980 (4 percent thereafter). These predictions are now in the process of major revision in view of the declared Federal government goal to attain U.S. self-sufficiency in domestic energy supply to meet future demands.

The transportation sector, which is almost entirely dependent now on liquid petroleum products, will be profoundly affected by the U.S. energy self-sufficiency goal. The transportation energy demand in the future may be substantially lower than that predicted by various sources quoted in this report. Such a reduction in demand will not be a simple task to implement and will require major readjustment in energy use in the transportation sector as well as in other sectors utilizing petroleum products. For example, the import of petroleum in 1973 rose to 35 percent of the total U.S. petroleum demand, exceeding previous predictions, and it would probably be in the 50 percent level in 1985 if the demand growth is permitted to continue. This important forecast is shown in Figure 1-2, which illustrates the widening gap between domestic

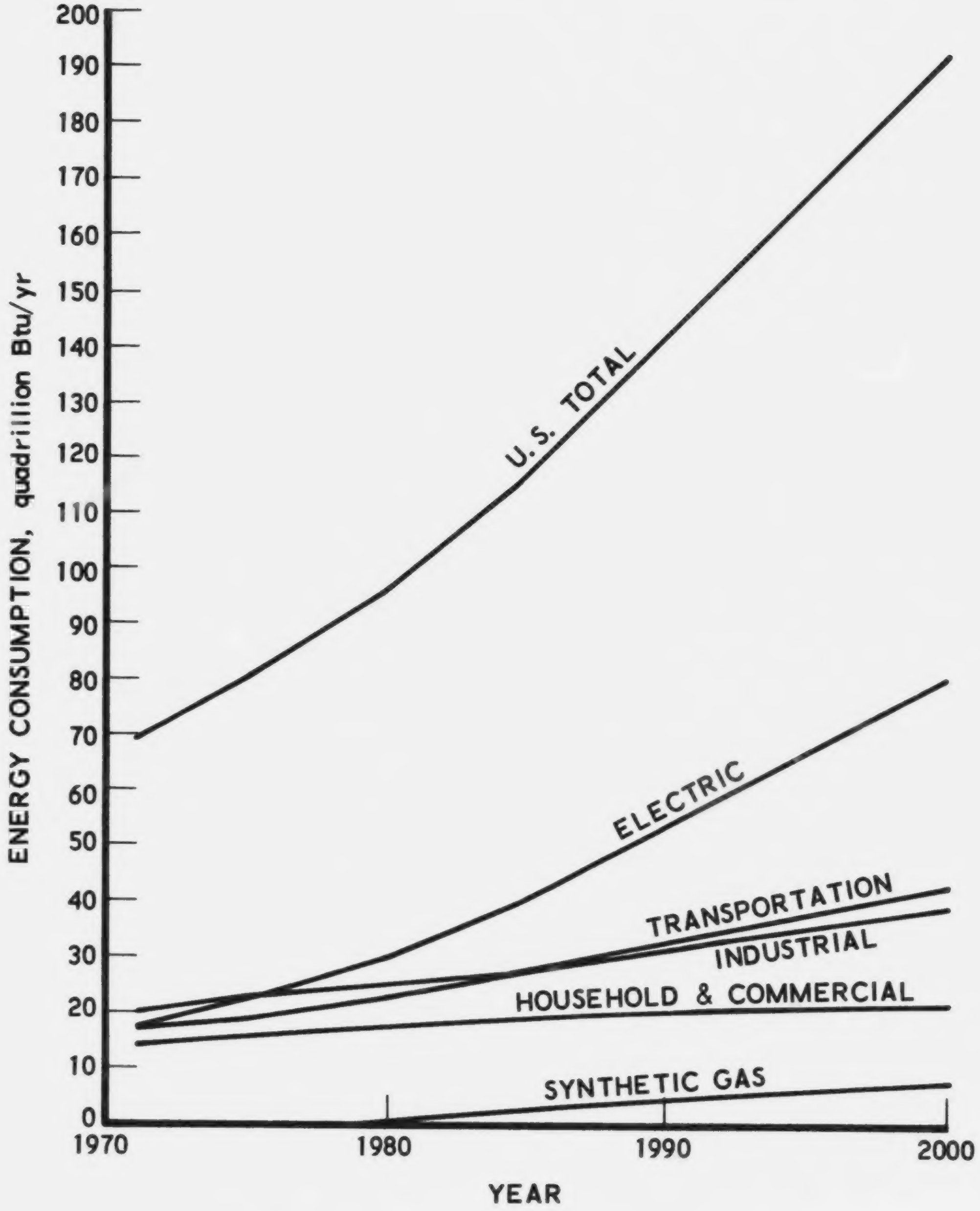

Figure 1-1. U.S. Energy Consumption by Sector (Ref. 1-1)

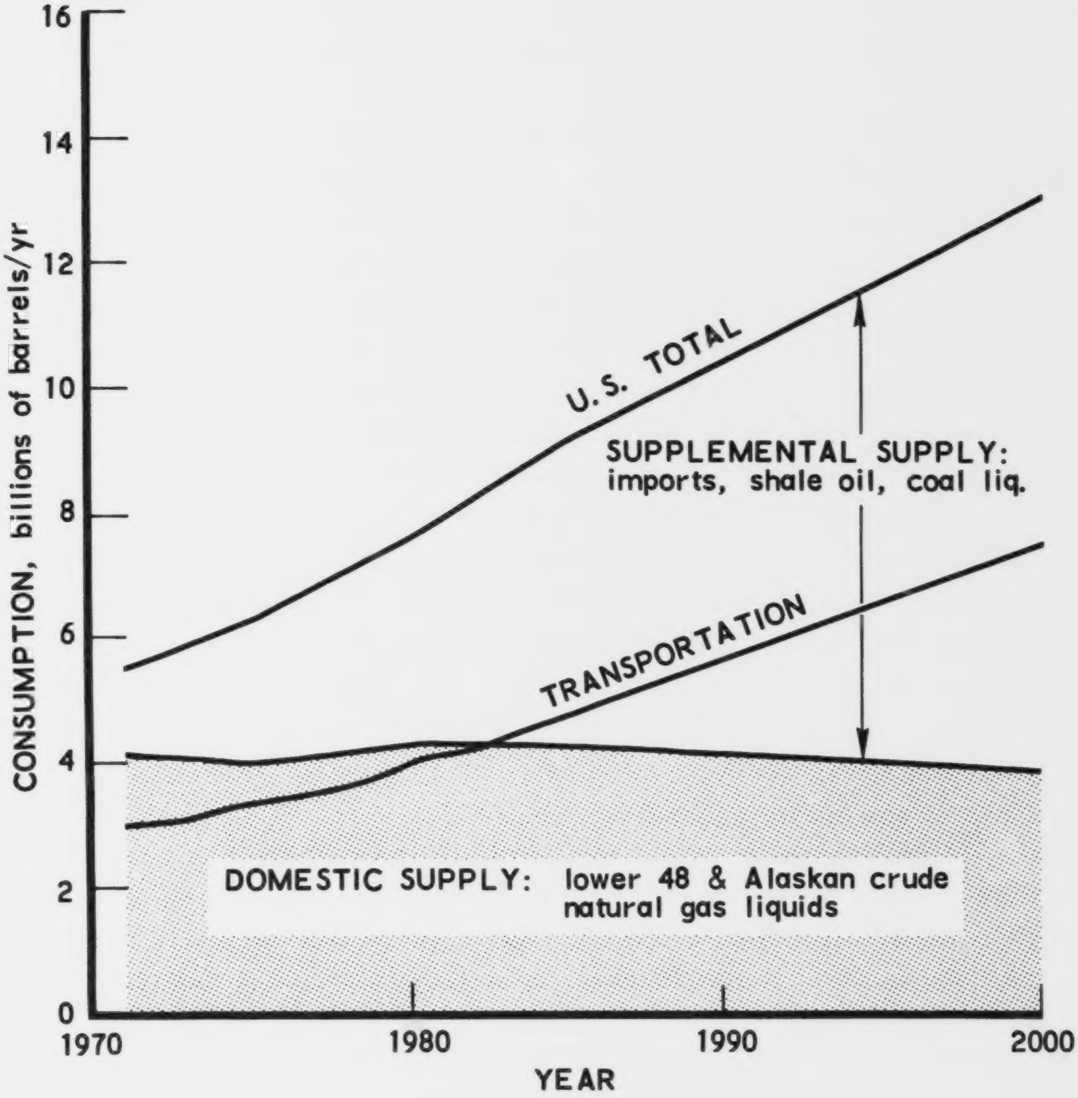

Figure 1-2. Petroleum Consumption/Supply Forecast (Ref. 1-1)

supply and U.S. demand. A similar situation exists with respect to gaseous fuels (see Figure 1-3), although the main demand for this fuel is not in the transportation but in the residential, industrial, and electrical sectors. It becomes clear, therefore, that a drastic reversal in the prior trends is necessary to meet the President's declared national goal of energy self-sufficiency in the 1980s.

With this in mind, the reader is advised to view the fuel supply and demand predictions quoted in this report with caution, realizing that dramatic changes are taking place in the energy picture. On the other hand, the changing energy situation will not substantially affect the state of the art, the performance characteristics, or the availability in their natural state of alternative fuels, and these can be used as a base for future predictions.

A pictorial guide is presented in Figure 1-4 for helping the reader progress through this alternative fuels volume. A brief review of energy sources in Section 2 defines, in general, the energy base of each of the alternative fuels. Then the status of the production process development of each fuel is briefly described in succeeding sections of the report. This is accompanied by a review of the expected near-term (1975 to 1985)* and far-term (1985 to 2000) availability of the fuel, including information on the current and projected production rates and consumer costs. A principal data source used was the two EPA/AAPS-funded studies (with the Institute of Gas Technology and Exxon Research and Engineering Company) related to the assessment of alternative automobile fuels.

Addressed next is a review of the applicability of a given alternative fuel to automotive engines. This includes evaluation of: (1) compatibility with various engine cycles, (2) fuel economy, (3) emission characteristics, (4) toxicity, (5) distribution, (6) storage, (7) safety, and (8) consideration of those factors inhibiting production and market introduction. From this review, research and development needs are identified, and the projected status of alternative fuels for transportation use in both the near-term and far-term periods is presented.

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*Exxon and IGT designations were near term (1975-1985), mid-term (1985-2000), and far term (beyond 2000).

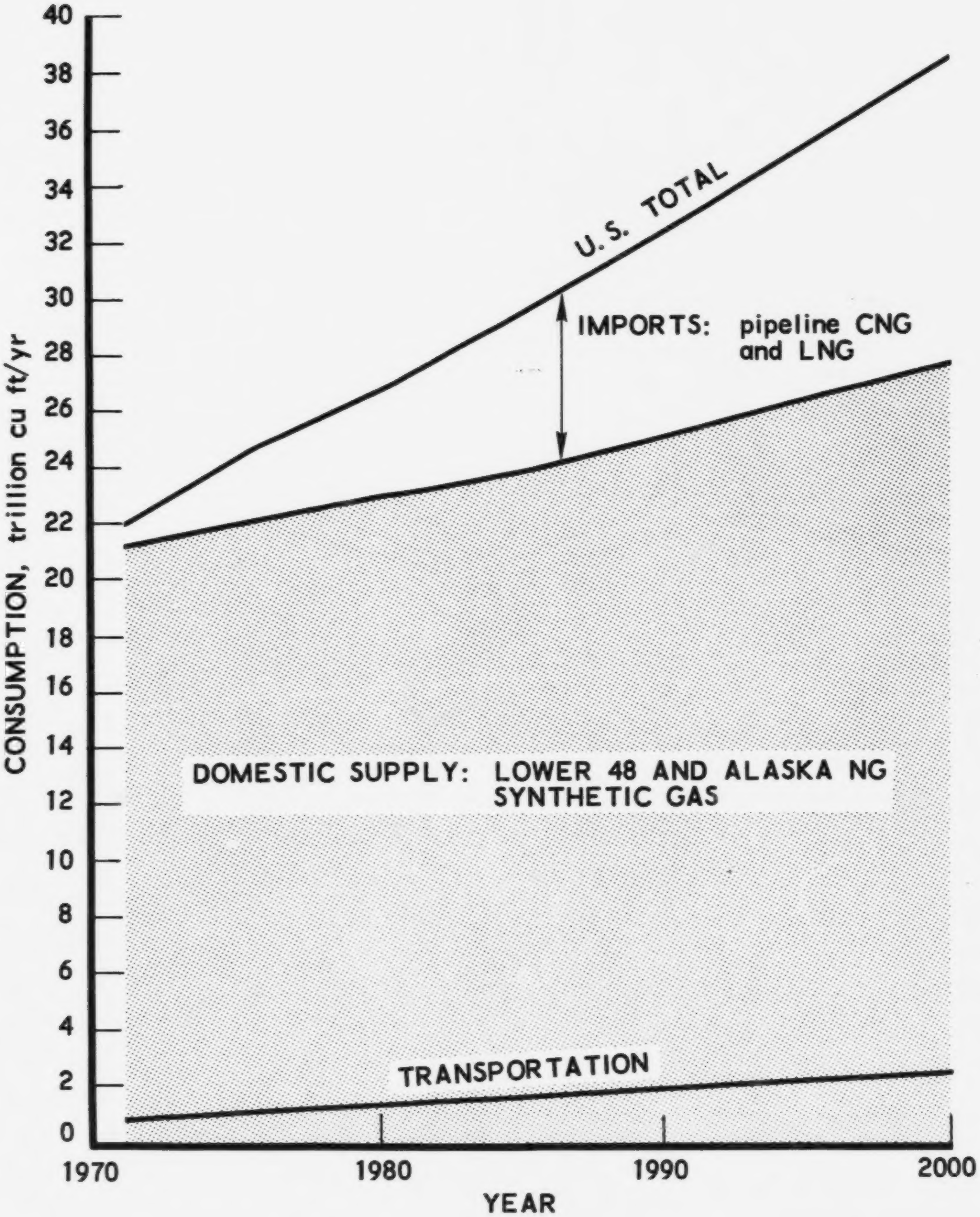

Figure 1-3. Gaseous Fuel Consumption/Supply Increase (Ref 1-1)

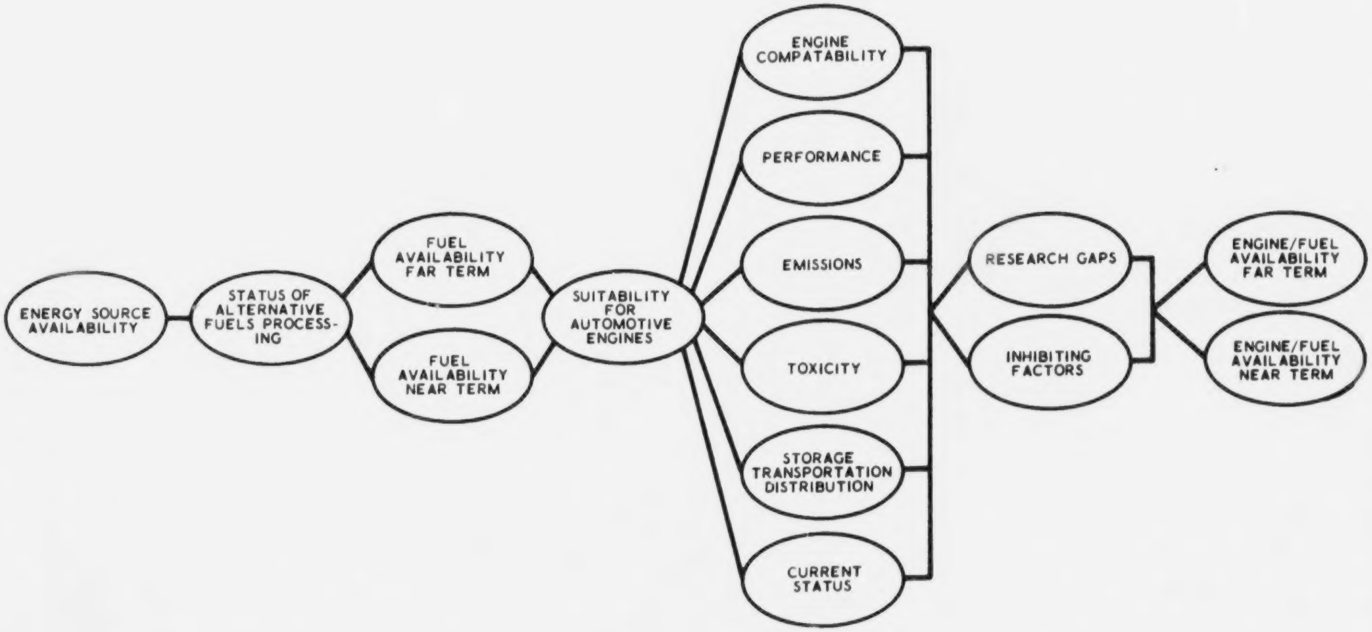
ENERGY SOURCE AVAILABILITY
STATUS OF ALTERNATIVE FUELS PROCESSING
FUEL AVAILABILITY FAR TERM
FUEL AVAILABILITY NEAR TERM
SUITABILITY FOR AUTOMOTIVE ENGINES
ENGINE COMPATABILITY
PERFORMANCE
EMISSIONS
TOXICITY
STORAGE TRANSPORTATION DISTRIBUTION
CURRENT STATUS
RESEARCH GAPS
INHIBITING FACTORS
ENGINE/FUEL AVAILABILITY FAR TERM
ENGINE/FUEL AVAILABILITY NEAR TERM

Figure 1-4. Alternative Fuels - Guide to Topics of Discussion

SECTION 2

TRANSPORTATION ENERGY RESOURCE OVERVIEW

In evaluating the viability of alternative (other than liquid petroleum-based) fuels for meeting automotive transportation needs, it is pertinent to provide an overview of the current energy picture for the U.S. and a projection of future energy supply and demand. It is the purpose of this section to provide such overview.

Of necessity, this report draws on published information and projections. It should be recognized, however, that published projections of the domestic energy future were based on an extrapolation of trends that are undergoing revision or change in fundamental ways. Hence, it is necessary that we factor uncertainty into our concepts of the future to a much greater degree than we have done in the past.

2.1 ENERGY SUPPLY VERSUS DEMAND

To attain a better insight into the U.S. energy balance (i.e., the comparison of predicted supply versus demand), three cases of supply (optimistic, intermediate,and pessimistic) and three cases of demand (low, intermediate, and high) are shown in Table 2-1. In all cases shown in Table 2-1, there is a deficiency in the domestic energy supply caused by increasing demand in energy coupled with the limited utilization of alternative forms of domestic energy (such as coal) by consumer sectors (industrial, electrical,and transportation). However, greater energy shortages have developed since these projections were made, and a number of conservation measures are already in effect to reduce current demand levels. In addition, significant increases in energy costs are beginning to impact on demand. The impacts are both direct and indirect (e.g., accentuating the demand for small cars while deflating the demand for large automobiles). The duration and degree of the current fuel supply limitations are not known; but, even when the

Table 2-1. U.S. Energy Balance (Refs. 2-1, 2-2)
All Units: Btu/Year × 10^{15}

Item / Year	Domestic Supply Available		Consumer Demand		Deficiency in % of Domestic Supply
	Level	Amount	Level	Amount	
1970	Actual	59.42	Actual	67.83	14.1
1975	High Case I	67.00	Low	80.50	20.0
	Interm. Case II	66.69	Interm.	83.48	25.0
	Low Case IV	61.79	High	85.82	38.9
1980	High Case I	86.42	Low	95.70	10.7
	Interm. Case II	82.85	Interm.	102.58	23.8
	Low Case IV	63.95	High	105.30	64.6
1985	High Case I	111.49	Low	112.50	9.1
	Interm. Case II	100.42	Interm.	124.94	24.4
	Low Case IV	77.59	High	130.0	67.5
2000*	Interm.	137.2	Interm.	191.9	28.5

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*From Ref. 1-1

limitations are removed, it is possible that a permanent and more modest pattern of energy consumption will have been established.

The energy deficit shown in Table 2-1 must be made up primarily by import of liquid petroleum and gas. In 1971 this import amounted to 26 percent for liquid petroleum and 4 percent for gas (expressed as percentage of each fuel total supply), but it has been estimated to increase by 1985 to 53.4 percent and 19.3 percent, respectively, and by 2000 to 70.3 percent and 28.2 percent, respectively (Ref. 1-1). The latter two sets of figures for liquid petroleum include relatively small quantities of liquids obtained from domestic oil shales or coal liquefaction.

2.2 ENERGY SUPPLY

One estimate of the U.S. energy resource base (Ref. 2-1) is shown in Table 2-2. According to this reference, coal is the largest single earth-bound energy source, followed by uranium (with nuclear breeder reactors) and oil shale. Solar energy requires a technological breakthrough before it can be used economically on a large scale; nuclear energy, based on breeder reactors, requires approximately 15 years development. Oil shale and coal resources require solution of environmental problems but are the most promising near-term available sources for energy growth. A brief review of some of these resources follows.

2.2.1 Coal

The domestic coal reserves are shown in Table 2-3. According to the U.S. Geological Survey, this country has 3,210 billion tons, of which 1,560 billon tons are mapped and explored at strip mining depths from 0 to 300 feet. Of this amount, approximately 150 billion tons are considered proven recoverable reserves, consisting of 45 billion tons of surface coal and 105-billion tons of below-surface coal (Ref. 2-2). With regard to sulfur content, 46 percent of the mapped and explored coal reserves (720 billion tons) have sulfur content ≤0.7 percent, while 93 percent of these low sulfur reserves are located in states west of the Mississippi River.

Table 2-2. U.S. Energy Resource Base (Ref. 2-1)

		(10^{15} Btu)				% of Total	
Resource	Btu/Unit	Assured	Reasonably Assured	Speculative	Total	a	b
Coal	25×10^6/ton	39,000	41,200	–	80,200	55.7	41.8
Crude Oil	5.8×10^6/bbl	210	1,317	1,212	2,739	1.9	1.4
Natural Gas	1032/cf	273	672	512	1,457	1.0	0.7
Natural Gas Liquids	4.0×10^6/bbl	27	–	–	27	Negligible	
Oil Shale	5.4×10^6/bbl	116	1,517	7,916	9,549	6.6	5.0
Uranium:							
In burner reactors w/o Pu recycle	400×10^7/ton	250	400	–	650	0.4	–
In breeder reactors	30×10^{12}/ton	18,750	30,000	–	48,750	–	25.4
Thorium	–	–	–	–	–		
Hydropower (Annual)	10.5×10^3/kw-hr	5.5	–	–	5.5	Negligible	
Geothermal (Annual)	–	4.0	4.0	–	8.0	Negligible	
Tar Sands	5.4×10^6/bbl	–	127	–	127	0.1	0.1
Nuclear Fusion	–	–	–	–	–		
Solar Energy (Annual)	17 watts/ft^2	49,056	–	–	49,056	34.1	25.5
Tidal Energy (Annual)	–	–	10.5	–	10.5	Negligible	
Wind Power (Annual)	–	5.4	–	–	5.4	Negligible	
		88,946.9- 107,446.9	45,247.5- 74,847.5	9,640	143,834.9- 191,934.9		

[a] Uranium in burner reactors w/o Pu recycle

[b] Uranium in breeder reactors

Table 2-3. Domestic Coal Resources (Refs. 2-2 and 2-3)

Depth of overburden (feet)	Type of Coal	Tons x 10^9	Energy, Btu x 10^{18}	
0 - 100 (strip mining)	Sub-bituminous and lignite	139.97	3.56	Mapped and explored - 1560 x 10^9 tons; unmapped - 1650 x 10^9 tons.
100 - 3000 (underground mining)	Bituminous	959.29	24.94	
	Lignite	447.64	11.64	
	Anthracite	12.97	0.34	
3000 - 6000 (underground mining)	All types	337.10	8.76	
8000 - 9000 (underground mining)	All types	1313.10	34.14	
	TOTAL	3210.10	83.40	

Location of proven recoverable reserves: 105 x 10^9 tons underground; 45 x 10^9 tons surface (<5% of total estimated).

Sulphur content: 46% of explored (720 x 10^9 tons) sulphur ≤ 0.7%; 93% west of Mississippi.

Although coal reserves appear ample, it is also important to consider the rate at which they could become available to meet demands for both raw coal itself and derived synthetic fuel. In Reference 2-2, several cases of supply rates were examined and the most optimistic forecast, Case I, is shown in Table 2-4. An annual growth rate of 5 percent was assumed for the domestic market until 1985 and 3.2 percent in the period 1985 to 2000. The export rate increased annually at a rate of 4.2 percent until 1985 and 3.2 percent thereafter. Table 2-4 also shows for comparison a less optimistic, intermediate supply forecast taken from Reference 1-1 with an average annual growth rate of 4 percent until 1985 and 2.7 percent thereafter. Excess of coal supply over domestic demand allows for an annual export of 9 to 12 percent of the total annual supply through the year 2000.

There is, however, considerable uncertainty concerning future U.S. coal exports. On the one hand, foreign importers of U.S. metallurgical coal are developing technology to reduce the need for coal and coke in steel making. On the other hand, constraints on the availability of petroleum to these importers make it possible that U.S. exports of steam coal will increase. The export value of coal and related products is at the billion dollar level and will increase significantly in the future, thereby providing a partial offset to the cost of importing other materials.

Considering these factors, it appears reasonable to assume that the average coal export level will be approximately 10 percent of domestic production. At this level, the exports would not constrain the availability of coal for the production of synthetic fuels. This inference may be strengthened by reasoning that synthetic fuel production will be based primarily on Western or Midwest coals, whereas coal exports are likely to be primarily from Eastern mines.

Both optimistic and intermediate coal supply forecasts (Ref. 2-2) point out problem areas that can influence actual future output. These considerations include: environmental concern over strip mining and sulfur dioxide emissions from power plants, availability of capital to open

Table 2-4. Coal Potential Domestic Supply (Ref 2-2, Case I)

Units - Tons/year x 10^6

Year		1970	1975	1980	1985	2000*	Overall Growth Rate %
Conventional Market		519.0	665	851	1093	1700	5.0 (3.2)**
Syn-thetic Fuels Demand	Gas	0	0	48	232	360	-
	Liquids	0	0	12	107	166	-
Exported to Other Countries		71.0	.92	111	138	214	4.5 (3.2)
TOTAL SUPPLY		590.0	757	1022	1570	2440	6.7 (3.2)

FOR COMPARISON, INTERMEDIATE CASE (Ref. 1-1)

Units - tons/year x 10^6

TOTAL SUPPLY	568.8	636	740	980	1418	4.0 (2.7)

*Extrapolated from Ref. 2-2

**( ) Refers to growth rate in the period 1985 to 2000 new mines, environmental acceptability of high-sulfur coal, reclamation of strip mining areas, and possible shortages of trained miners as well as supervisory and professional personnel.

The environmental problems associated with coal mining and with construction and operation of coal gasification plants are being investigated in detailed studies to evaluate this problem. The plant effluents considered necessary to control are noxious gases generated during gasification processes (such as hydrogen sulfide, sulfur dioxide, and oxides of nitrogen); combustion and sulfur recovery operations; liquids consisting of processed waste waters contaminated with phenols, ammonia, oil, and tars; and solids consisting of fine coal dust and char. The plan for either disposal of the wastes as byproducts or conversion into useful products must be made before a facility is constructed and before an environmental impact statement can be submitted to the appropriate agency.

Coal gasification research in the United States during the last 10 to 15 years has been funded by the Office of Coal Research, the Bureau of Mines, the American Gas Association, and private industry. Over $71 million has been spent on this research. In addition to these funds, an accelerated research program was started with joint funding of the Department of the Interior and the American Gas Association. The project will involve expenditure of approximately $300 million over the next eight years.

The cumulative investment cost of coal gasification plants is estimated to be approximately $10 billion to 12 billion. When additional costs are added for coal mines, water supply, and environmental control requirements, total costs ranging from $20 billion to $25 billion are possible. Such investment funds may be difficult to raise in light of the high risks associated with new processes and plants for the energy industry, and there may be need for a government subsidy or for participation of the oil-producing nations themselves.

2.2.2 Oil Shale

Turning now to the question of oil shale resources, Reference 2-2 contains a detailed analysis of availability. Deposits of potential commercial interest exist in the Green River Formation of Colorado's Piceance Basin. Of the 1,781 billion barrels of potential resources, only 129 billion barrels are accessible, well-defined, and sufficiently rich (30 to 35 gallons per ton by assay). Furthermore, the amount that can be recovered by proven technology (which starts with extraction of a minable seam) will be considerably less than the gross resource estimate. The most economically recoverable portion of the Green River Formation is calculated to be equivalent to 54 billion barrels of synthetic crude. Less than 6 billion barrels are forecast to be recovered through 1985 under the maximum feasible production growth (Ref. 2-2). This corresponds to a production capacity of 150,000 barrels per day by 1980 and 750,000 barrels per day by 1985. Production by the year 2000 could reach about 2 million barrels per day.

Unlike coal, the organic material, kerogen, in shale shows much less variability in composition with geographical location. It is typically composed of 80 percent carbon, 10 percent hydrogen, 1 percent sulfur, with oxygen and nitrogen making up the balance. The hydrogen-to-carbon ratio is higher than in most coals, so that about two-thirds of the kerogen can be converted to oil simply by heating. Processes for oil shale treatment are more nearly ready for use than those for coal liquefaction. However, the crude yield from coal is much greater: 3 to 3.5 barrels per ton of coal versus 0.8 barrel per ton of shale for relatively rich oil shale (Ref. 1-1).

There are a number of factors that can influence the future level of production. Federal leasing policies are of utmost importance because about 80 percent of the oil shale resources of the Green River Formation are federal holdings. Environmental controls, particularly on the disposal of spent shale, fines, and contaminated wastes, can either delay project startup or add substantially to product costs. Over the long term, water availability may be a limiting factor, although sufficient water for mine and plant use is available for the maximum anticipated scale of oil shale crude production up to 1985. (Approximately 150 gallons of water per barrel of shale crude is required for mining and extraction.) Technological improvements in mining and oil production will likely occur as industry experience develops. Development of feasible and economic in-situ methods are important for recovery of the deeply buried shale deposits. The growing impact of fossil fuel price escalation will, no doubt, be an incentive in the development of oil shale production processes. Of interest is the recently announced oil shale projects of Union Oil and ARCO/TOSCO/Ashland in which a 50,000-barrel-per-day plant will be constructed in the Piceance Basin of western Colorado with operations starting in 1977.

2.2.3 Tar Sands

Domestic tar sands of potential commercial value have been identified in only five deposits in Utah, with total estimated in-place resources ranging from 18 to 28 billion barrels. These estimates are based on very sketchy data and may be overstatements. Based upon available information on resources, technology, and likely costs, the conclusion is that the total possible rate of output from domestic tar sands would be minimal even to the year 2000 (Ref. 2-2), mainly because the cost of extracting fuel from domestic tar sands is expected to be significantly higher than the cost of producing alternative domestic synthetic fuels, and because the technology being developed for extracting fuel from Canada's Athabaska tar sands may not be applicable to U.S. deposits.

2.2.4 Solid Waste

The last potential source of synthetic hydrocarbon fuel to be considered is solid waste. The U.S. unquestionably generates large quantities of solid wastes, about 1.1 billion tons of inorganic mineral wastes and more than 2 billion tons of organic wastes each year. As recently as 1971, waste conversion proponents argued that treatment of this organic waste could produce nearly 2.5 billion barrels of oil per year, roughly half this country's total oil consumption in that year (Ref. 2-4). A study prepared for the U.S. Department of Interior's Bureau of Mines by the University of Utah (Ref. 2-5) indicates that more than half the total waste is absorbed water. The total amount of dry, ash-free organic waste was actually 880 million tons, of which more than 80 percent was so widely dispersed that it could not be readily collected. Typical constituents are manure, urban refuse, logging and wood manufacturing residues, agricultural crop and food wastes, industrial wastes, and municipal sewage solids. Because energy is required for both the collecting and processing of wastes, there are thermodynamic as well as cost limitations to what can be collected and how far it can be transported to a processing plant. Readily collectable annual wastes could have produced 170 million barrels of oil, roughly three percent of 1971 U. S. total crude oil consumption or 12 percent of imported crude oil. It appears that, while conversion of organic wastes to fuel is an ideal way to dispose of the wastes, it would not have a significant impact on relieving energy deficits.

2.2.5 Uranium

Uranium can be a substantial energy source in the year 2000 if the fast breeder reactors with fuel doubling time of eight to ten years (Ref. 2-2) come into operation in the period starting in the period starting in 1990. The rate of uranium utilization for electric power generation depends on the number of regulatory and environmental constraints. Predictions made for the electrical sector (which will depend increasingly on nuclear energy) indicate that it is the fastest average annual growth sector (Ref. 1-1), exceeding the rate of total energy demand; the difference in growth rate is expected to decrease as the fraction of total energy contributed to electricity increases. To illustrate the dramatic predicted growth in nuclear power plants, Reference 1-1 quotes approximately 9,000 megawatts installed in 1972; 215,000 megawatts predicted in 1985; and 960,000 megawatts in the year 2000.

2.2.6 Solar Energy

Solar energy received in the U.S. amounts to 4.9×10^{19} Btu per year (see Table 2-2), but conversion of it to useful form is difficult with present technology. Use of photovoltaic methods with 10 percent conversion efficiency would require about 15 square miles for a 1,000-megawatt plant (Ref. 2-6). On a smaller scale, experiments with solar cells and heat pumps are being conducted for residential dwellings. Another approach lies in placing hugh solar cell platforms in earth synchronous orbit and transmitting the energy to earth by microwave radiation, but this appears to be economically unfeasible. Clearly, for significant utilization of this energy source a new technological approach to the conversion of solar energy is required.

2.3 ENERGY DEMAND

2.3.1 Industrial Sector

The industrial sector used fossil fuels (petroleum, natural gas, and coal) for 89.6 percent of its energy requirement in 1971; it is estimated that this sector will use fossil fuels for 82 percent of its energy requirement in 1985 and 73 percent in the year 2000 (Ref. 1-1). The participation of coal in meeting its energy needs decreased from 19.7 percent of requirements in 1971 to a forecast of 11.6 percent in 2000. The balance is taken up by an increased amount of electricity purchased (from 10.7 percent in 1971 to 27 percent in 2000) (Ref. 1-1). The desired trend here would be the maintenance of 20 percent of coal participation which would reduce the demand for liquid petroleum products. This would be reflected, for example in a reduction in liquid petroleum imports needed for the year 2000 by about 13 percent.

2.3.2 Electrical Generation Sector

The electrical generation sector is characterized by a predicted tremendous growth in nuclear energy from 2.3 percent of total installed electric capacity in the U.S. in 1971 to 61 percent in the year 2000 (Ref. 1-1). Simultaneously, the fossil fuel contribution in this sector is predicted to decrease from 82 percent in 1971 to an estimated 31 percent in the year 2000. In spite of that decline, fossil-fuel energy expenditures in the year 2000 are 1.75 times that of 1971 (Ref. 1-1).

The referenced forecast predicts a growing participation of coal and a gradual decline in petroleum after 1985. One of the anticipated improvements would be a faster transition from petroleum and gas to coal in the 1975 to 1985 period. Another would be acceleration in the development of industrial production processes for coal liquefaction and gasification.

2.3.3 Transportation Sector

Transportation consumed approximately 25 percent of the U.S. total energy demand in 1970 and most references predicted only a slight decrease to approximately 22 percent in the year 2000, as shown in Table 2-5. It uses at present approximately 55 percent of U.S. liquid-petroleum (Refs. 2-7 and 2-8), with 95 percent of its energy coming from liquid petroleum, 4.9 percent from natural gas and 0.1 percent from electricity (Ref. 1-1).

However, the projections were based on an extrapolation of trends that we now recognize as being unstable. The recognition of supply limitations and the implications of such limitations have resulted in a federal program of fuel allocations and priorities. The impact on the transportation sector is relatively large. It now appears possible that the absolute transportation energy demand growth may be much flatter than previously projected and may decline significantly as a percentage of a total energy demand.

2.4 PROJECTED STATUS

It can be concluded from the brief U.S. energy review that a competitive demand for liquid petroleum and natural gas will exist through the year 2000. Some easement in the shortage could be realized by an accelerated program of coal mining, coal liquefaction and gasification, and more rapid conversion toward coal usage of the industrial and electrical sectors.

The transportation industry is taking steps to reduce its fuel requirements. Table 2-6 shows that in 1969 just over half of the transportation energy was consumed by automobiles. Clearly, this is an area where improvements could be of national importance. A step in that direction would be the implementation of an improved mass transit system for intracity and intercity traffic. Although air transport is a smaller consumer, it could also produce significant economies by operating at higher load factors, lower per-trip fuel consumption, etc.

In the near term (1975 to 1985), improvements leading to a reduction in the use of liquid petroleum products could be realized by a

Table 2-5. Transportation Energy Demand
Units: Btu per yr x 10^{15}

Year	Level	Data Source			
		Reference 2-2		Reference 1-1	
		Amount	% of Total Domestic Demand	Amount	% of Total Domestic Demand
1970	Actual	16.2	24.0	16.97	24.6
1975	Low	19.3	24.0	19.07	23.8
	Inter.	20.0	24.0		
	High	20.5	24.0		
1980	Low	23.0	24.0	22.84	23.8
	Inter.	23.9	23.3		
	High	24.4	23.2		
1985	Low	26.7	23.7	27.09	23.2
	Inter.	28.3	22.6		
	High	29.0	22.3		
2000	Low	--	--	42.61	22.2
	Inter.	--	--		
	High	--	--		

Table 2-6. Distribution of Energy Consumption in Transportation by Mode (Ref. 2-1)

(1969 Ref. Year)

Overall Transportation Consumption: 15 x 10^{15} Btu per Year

Mode		Energy Source	Percent
Auto		Oil	51.2
Truck	(Intercity Freight)	Oil	9.1
	(Urban Freight)	Oil	5.1
	(Service and Utility)	Oil	8.2
Bus	(Intercity)	Oil	0.27
	(Urban and School)	Oil	0.54
		Subtotal	74.41
Rail	(Intercity Passenger)	Oil and Wayside Electric	0.14
	(Freight)	Oil	3.6
	(Subway)	Wayside Electric	0.14
Pipeline		Oil and Gas, Mostly	2.0
Air	(Passenger)	Oil	11.4
	(Freight)	Oil	2.6
Water	(Passenger)	Oil	0.27
	(Freight)	Oil	5.8

two-fold approach: one is an improvement in fuel economy of automotive vehicles by development of more efficient engine cycles and more efficient vehicles (those with reduced parasitic losses and reduced weight); the other is by application of alternative nonpetroleum-based fuels.

The problem posed in the distribution of alternative fuels for the transportation sector in particular cannot be overlooked because of the multiplicity of retail outlets required. The present distribution system for liquid petroleum products starts with oil wells, proceeds to refineries, then to terminal distribution centers, and from there to approximately 300,000 service stations throughout the U.S. This represents a multibillion-dollar investment. Alternative fuels that are compatible with this distribution system would utilize this investment, while, for other fuels such as natural gas, synthetic gas, or hydrogen, for instance, a new distribution system must be considered in evaluation of the total fuel economics.

In the far term (1985 to 2000), further diversification of energy sources for transportation may be possible by application of electrical energy to automotive vehicles. This will require a technology breakthrough in vehicle power train components; more efficient and economical energy storing devices (batteries) and lightweight motor/control packages are needed.

Each of the sections within this volume on alternative fuels contains estimates of capital investment required to produce these fuels. The impact of these costs can best be evaluated by comparing them with capital investments for gasoline refining. The following quotation referring to capital investment needs for petroleum refining was obtained from Reference 2-9:

> "U.S. refining must double annual investment to meet 1980 needs. C.F. Braun's Robert Skamser says the nation will need 67 new 150,000 barrels per day plants to provide the additional 10 million barrels per day of new refinery capacity required by then. Total cost of construction will exceed $18 billion ---"

Although the exact magnitude of the capacity additions [illegible] perhaps questionable in view of possible continuing limitations on the availability of imported crude oil, it may be inferred from the above figures that new investment in petroleum refining will average about $1,800 per daily barrel of crude charging capacity. Also (per Reference 2-9) as of March 1973 the daily average U.S. refinery runs were in excess of 12 million barrels per day. Based on current costs, the present capital investment in petroleum refining (assuming that operation is at 100 percent capacity) is estimated at approximately $22 billion. This investment is exclusive of the cost for storage and distribution.

The succeeding sections will examine the various approaches to the use of nonpetroleum-based alternative fuels in some detail by evaluation of (1) the characteristics of potential fuels in various automotive power plants, (2) the supply and economics of these alternative fuels and energy sources, and (3) the problems involved in their future application.

SECTION 3

SYNTHETIC GASOLINE AND DISTILLATE HYDROCARBON FUELS

3.1 CHARACTERIZATION

3.1.1 Fuel Type

This category includes a broad spectrum of hydrocarbon mixtures which are qualitatively similar to those in use today in the transportation sector. However, rather than being derived from petroleum sources, they would be manufactured from coal, oil shale, tar sands, or organic waste products. They possess the primary advantage of essentially complete compatibility with existing and advanced mobile combustion power plants as well as with distribution facilities down to the local gas station. On the other hand, they do not, in themselves, provide a path to reduced pollutant emissions.

There are five hydrocarbon fuels included in this category: gasoline, diesel oil, kerosene, naphtha,and No. 2 fuel oil. They are mixtures of hydrocarbons of four basic types, differing in their properties according to the number of carbon atoms in the molecule and in the arrangement of the atoms. The four types are: (1) paraffins — open chain, saturated as hexane, C_6H_{14}; (2) olefins — open chain, one double bond, as hexene, C_6H_{12}; (3) naphthenes — cyclic, saturated, as cyclohexane, C_6H_{12}; (4) aromatics — cyclic, unsaturated, as benzene, C_6H_6. The various hydrocarbon fuels differ in the proportions of, and specific compounds within, each type. To indicate the great number of possible compounds in this category, there are several hundred different hydrocarbons present in a single commercial gasoline. Because each type imparts certain specific characteristics to the final product, there are frequently specifications that directly or indirectly control the percentage allowed in the final product. In addition to the hydrocarbon compounds, there are usually minute quantities of impurities containing the so-called heteroatoms, sulfur, oxygen, and nitrogen that are carried over from the feed stock or introduced during processing. Also, various additives are employed to impart certain desired properties such as antiknock, detergent, and viscosity-control compounds.

Individual compounds, such as benzene, are not included in the list of candidate fuels in this section for several reasons. It is not economically feasible to convert the complex mixture in crude oil into one specific compound. Also, a single compound seldom possesses all the attributes of a good fuel.

A few properties of these fuels may serve to put them in perspective. The carbon-to-hydrogen weight ratio is on the order of 5.5 with lower heating values ranging between 18,500 and 19,300 Btu/pound. Specific gravity extends from 0.73 for gasoline to 0.86 for No. 2 fuel oil. Boiling points range from below 100°F for the low end of gasoline to near 650°F for the high end of fuel oil, illustrating the great diversity of compounds present in these fuels. A further discussion of physical and chemical properties is given in Section 3.1.4.

3.1.2 Reserves or Raw Material Sources

The fuels in this category have to date been obtained predominantly from petroleum sources; the only exception is the gasoline derived from natural gas liquids. Inasmuch as domestic sources are already inadequate to meet automotive requirements plus other fuel and nonfuel demands, attention has recently been focused on other domestic energy supplies. The primary potential sources of liquid hydrocarbon fuels are from the processing of either coal or oil shale. Additional domestic sources of much less potential in terms of ability to meet energy needs are tar sands and solid wastes. These sources were discussed in Section 2.

3.1.3 Methods of Manufacture

A brief digression at this point is worthwhile to review the steps in process development leading to commercial production. This review is intended to provide a better understanding of the current status of coal liquefaction and the magnitude of the task for the future. The earliest stage occurs in the laboratory, often termed bench-scale, where the pertinent chemical and physical principles are demonstrated, usually on a batch basis. Once scientific feasibility is shown, the process can be scaled up to pilot plant size to prove engineering feasibility, generally on a continuous basis. Hardware, machinery and control equipment can be tested and proven, processing alternatives evaluated, and yields confirmed here. At this point it is prudent, especially for a new technology such as coal liquefaction, to proceed to an intermediate stage, variously termed a demonstration, prototype or semicommercial plant. The primary purpose here is to determine the economics of a large-volume operation through verification of equipment durability, product yield and quality, adequacy of environmental controls, and such logistic support requirements as operating and maintenance manpower. At some point during this demonstration phase, the decision is made to commit a large capital investment to the construction of full-scale, probably multiple, production plants.

It is difficult to define a general size range in terms of either input or output quantities for each development stage, since it varies widely with the specific product involved. However, for coal or shale conversion, a rough breakdown would be:

- Bench scale - less than 1 ton per day raw material input
- Pilot plant - 1 to 200 tons per day
- Demonstration plant - 200 to 5,000 tons per day
- Commercial - greater than 5,000 tons per day

Production of clean liquids (or clean solids) from coal can be carried out by three principal routes. In the first route, clean gas containing appropriate proportions of CO and H_2 (synthesis gas) is converted by the Fischer-Tropsch process to hydrocarbon oil.

The second route involves heating the coal in the absence of air (pyrolysis), which breaks down the coal structure to the molecular weight range of oil. The oil is then treated with hydrogen for desulfurization and quality improvement. The major products from pyrolysis processes are gas plus char (~80 percent) rather than oil. The COED (Char-Oil-Energy-Development) Process of the FMC Corporation and TOSCOAL Process of The Oil Shale Corporation are based upon the pyrolysis approach. Pyrolysis produces an oil with a higher hydrogen-to-carbon ratio than in the original coal by rejection of carbon (char).

The third route to clean liquid fuels raises the H:C ratio by adding hydrogen. One approach is by direct hydrogenation in the presence of a catalyst, exemplified by the Synthoil Process of the Bureau of Mines, and the H-Coal Process developed by Hydrocarbon Research, Incorporated. Alternatively, a two-stage route can be used in which the first stage consists of a mild hydrogenation without a catalyst. After solids rejection, the extract may be further hydrogenated over a catalyst to yield a lower boiling distillate fraction. In the Consol Process of the Consolidation Coal Company, a donor solvent supplies most of the hydrogen in the first step, while in the Solvent Refined Coal Process, developed by the Pittsburgh and Midway Coal Mining Company, gaseous hydrogen at elevated pressure is employed. These processes are discussed in further detail in Section 3.1.3.1.

The chemical composition of the available coal greatly influences the processes that can be used, the equipment and operating conditions, the quantity and characteristics of the products produced, and the economics of the operation. Several feed coals are therefore included during process development; Pennsylvania State University is characterizing the composition, physical properties, and process behavior of over 300 U.S. coal samples (Ref. 3-1).

Several processes are being investigated to make liquid hydrocarbon fuels from coal, some in commercial production outside the United States, others in the development stage or on a pilot-plant scale. The least thermally efficient or economically attractive process is the one with the longest history of commercial utilization, viz., the Fischer-Tropsch process. The Sasol installation in South Africa has been producing small amounts of synthetic liquid hydrocarbons for over 20 years, based upon German technology that was commercialized between 1925 and 1945. The first step is the generation of purified synthesis gas, primarily, $CO + H_2$. The Lurgi process is used at Sasol, but others are possible as shown in Table 3-1. The synthesis gas then contacts an iron catalyst in either a fixed-bed or fuild-bed synthesis are straight-chain, high-boiling hydrocarbons with some medium boiling oils, diesel oil, LPG, and oxygenated compounds. Products from the fuild-bed reactor are mainly low boiling hydrocarbons (C_1 - C_4) and gasoline, with a little medium and high boiling material.

Turning now to the production of synthetic liquid fuel based upon coal pyrolysis, several processes are under development, principally the COED and TOSCOAL approaches described in the following paragraphs.

3.1.3.1 COED Process Description

The COED (Char-Oil-Energy-Development) process produces synthetic crude oil by pyrolysis of coal (see Figure 3-1). Coal is crushed to minus 1/8 inch size, dried, then heated to successively higher temperatures in a series of fluidized-bed reactors. In the first stage the coal is heated to 600°F by hot flue gases and devolatilized. In the subsequent stages the coal is subjected to increasing temperatures of 850°, 1000° and 1600°F. The pressure of the operation is between 6 to 10 psig. Some of the char is burned with oxygen in the fourth stage to maintain the 1600°F temperature in that stage and to provide the hot gases for heating the second and third stages. Gas from the fourth stage flows countercurrent to the solids through the third to the second stage, from which most of the volatile products are collected.

Table 3-1. Coal to Synthesis Gas (H_2 + CO) (Ref. 3-2)

Energy/Material Resources	Name of the Process	Comment on the Process	Synthesized Fuel	By-Product	Thermal[a] Efficiency, %	Comments on Pollution
1 ton coal 6470 SCF O_2 1687 lb high-pressure steam 210 gal. process water	Lurgi Pressure Gasifier	Operated at 450 psi and 1400°-1600°F high-ash coal (7500 Btu/lb)	46,000 CF raw gas 30,000 CF purified gas (400 Btu/SCF)	0.5 gal. oil 2.9 gal. tar 321 gal. gas liquor 1551 lb low-pressure steam	77	Relatively low off-gas temperature and countercurrent design increase appearance of tars, NH_3, etc., in waste quench liquor.
1 ton coal 20,376 SCF O_2 708 lb low-pressure steam 83.8 kWhr	Kopper Totzek Process	Operated at 1 atm and 1830° to 2370°F carbon conversion 96% high-ash coal	56,600 CF raw gas (277 Btu/SCF)	2374 lb steam NO 4.5 ppm	71	Very high off-gas temperature precludes the formation of any compound less stable than H_2, CO, CO_2.
1 ton coal [illegible],271 SCF O_2 3100-lb low-pressure steam	Winkler Generator	Operated at 1 atm and 1470° to 1650°F carbon conversion 80% low-ash coal (976 Btu/lb)	52,200 CF raw gas (288 Btu/SCF)	1500 lb steam at 17.6 atm	65	High gasifier temperature ensures that all tars and heavy hydrocarbons are reacted.
1 ton coal 14,050 SCF O_2 261-lb low-pressure steam	Rummel Single-Shaft Slag Bath Gasifier	Operated at 1 atm and 1830°F (coal 10,025 Btu/lb) carbon conversion 99%	49,300 CF CO + H_2	2064 lb steam	78	The reactants pass through slag, consequently off-gas contains relatively high amounts of ash.
1 ton coal 19,950 SCF O_2 2390-lb low-pressure steam	Flesch Demag Generator	Operated at 1 atm and 570°-750°F high-ash coal (13,400 Btu/lb) pilot-plant scale	65,400 CH CO + H_2	987 lb steam	66	Process is good for low reactivity fuels and fuels with a low-ash fusion temperature.
1 ton coal 18,380 SCF O_2 1680-lb low-pressure steam	Wurth Gasifier	Operated at 1 atm and 715°F, coal (12,375 Btu/lb)	71,900 CF CO + H_2	--	75	--
1 ton coal 19,160 SCF O_2 610 lb steam	U.S.B.M. Gasifier	Operated at 20 atm and high temp. Coal (12,950 Btu/lb) pilot plant	51,800 CF CO + H_2	1539 lb steam	60	Heat losses in the gasifier are high. Produced gas contains less heavy hydrocarbons because of high temperature of the gasifier.
1 ton coal 19,950 SCF O_2 1750-lb steam	B&W-DuPont	Operated at 1 atm and 2190°F, coal (14,480 Btu/lb)	59,000 CF CO + H_2	3500 lb steam	65	Two high-temperature reaction zones ensure that all tars and heavy hydrocarbons are reacted.
1 ton coal 20,570 SCF O_2 3000-lb steam	IGT Gasifier	Operated at 5 atm and 2700°F, coal (12,140 Btu/lb) pilot-plant scale +Cold gas efficiency	62,900 CF CO + H_2	--	63+	Very high off-gas temperature precludes the formation of any compound less stable than H_2, CO, CO_2.

[a] Thermal efficiency based upon high heating value of input and output streams, including by-products.

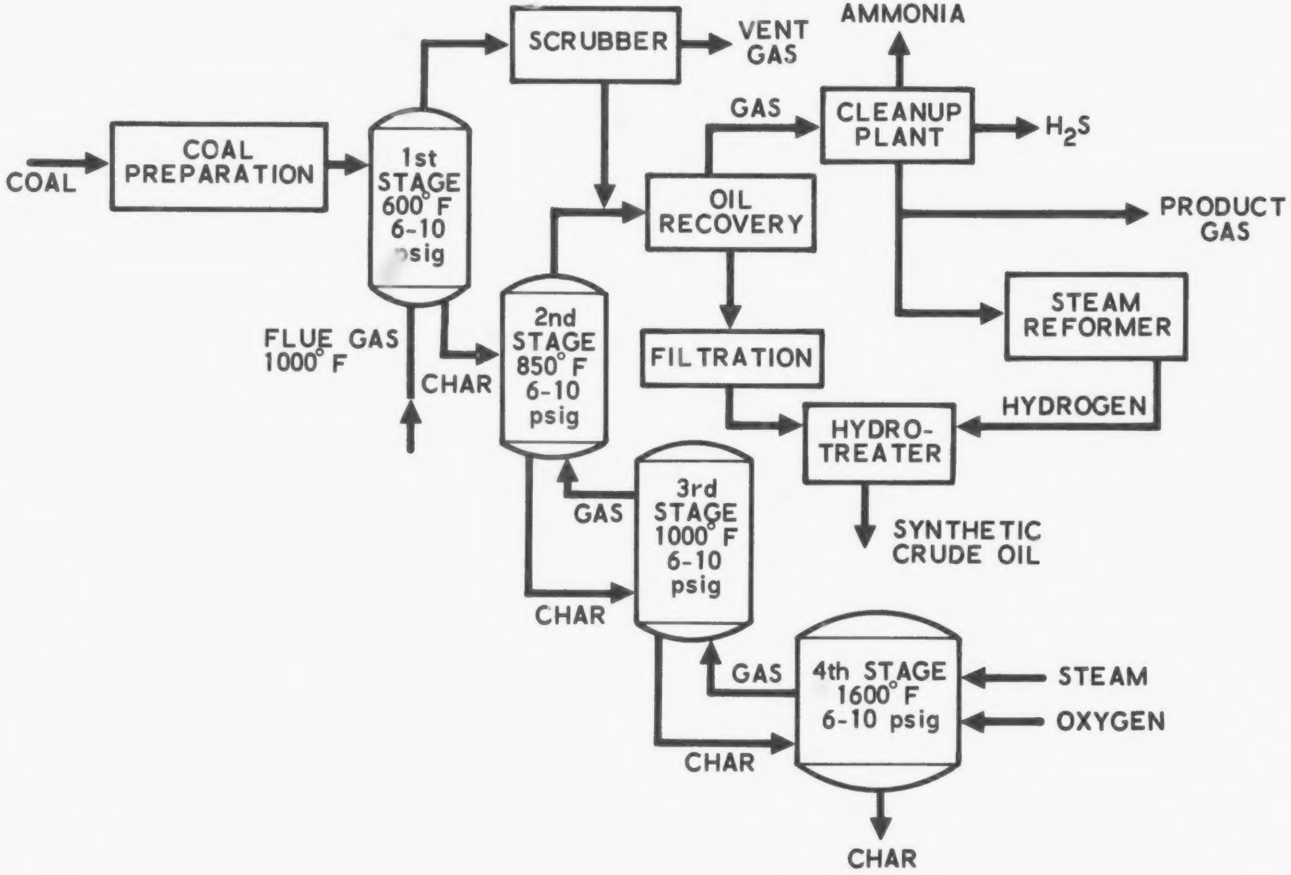
COAL
COAL PREPARATION
1st STAGE 600° F 6-10 psig
FLUE GAS 1000° F
CHAR
SCRUBBER
VENT GAS
2nd STAGE 850° F 6-10 psig
CHAR
GAS
OIL RECOVERY
GAS
AMMONIA
CLEANUP PLANT
H2S
PRODUCT GAS
STEAM REFORMER
FILTRATION
HYDROGEN
HYDRO-TREATER
SYNTHETIC CRUDE OIL
3rd STAGE 1000° F 6-10 psig
GAS
CHAR
4th STAGE 1600° F 6-10 psig
STEAM
OXYGEN
CHAR

Figure 3-1. COED Process (Ref. 3-3)

Exit gas from the first stage is quenched with recirculating liquor, and oil is recovered. Part of the gas is used in the coal drier and part in the char cooler. Volatile products in the second-stage gas proceed to the product recovery section. The gas is quenched directly with water to condense the oil. The oil is separated from water and filtered to remove char carryover. Separator gas from the oil recovery section is purified to remove ammonia, CO_2, and H_2S and is then steam reformed to produce hydrogen. The filtered synthetic crude oil is minus 4^{o} API*, a solid at room temperature. Hydrotreating at about $750^{o}F$ and 1500-3000 psig removes sulfur, nitrogen, and oxygen from the oil and produces a 25^{o} API synthetic crude oil.

- Typical Products

  Some yield data for pyrolysis of Illinois No. 6 seam coal.

	Net Process Yield	Net Yield From Coal Pyrolysis, Weight % of Dry Coal
Char	1177 lb/ton	59.1
Oil	1.04 bbl/ton	19.6
Liquor	7.1 gal/ton	5.5
Gas	8133 SCF/ton	15.8
TOTAL		100.0

After acid gas removal, the pyrolysis gas will typically have a composition of 50 percent H_2, 32 percent CO, 10 percent CH_4, 8 percent other. The portion of this gas not required for hydrogen production might be converted by methanation to high Btu pipeline gas. This modification is refered to as the COGAS process.

$$^{*}\ ^{o}API = \frac{141.5}{\text{sp. gr. at } 60^{o}\text{ F}} - 131.5$$

- Current Status

A pilot plant with a capacity of processing 36 tons of coal per day has been operational since December 1970 near Princeton, New Jersey. Design capacities have been achieved on all parts of the pilot plant with significant accomplishments being demonstrated in solids circulation between multiple fluidized bed reactors, in the filtration of coal oil, and in upgrading the coal oil to synthetic crude oil through fixed bed hydrotreating. The product oil is being refined by several petroleum companies: FMC Corporation is investigating private backing for a commercial plant by 1980 (Ref. 3-4). The Navy has tested the fuel oil at sea. Research is directed toward utilizing the high-sulfur chars obtained from high-sulfur coals.

3.1.3.2 TOSCOAL* Process Description

The basic feature of this pyrolysis process is to provide the required heat by using hot ceramic balls (see Figure 3-2). Coal is crushed, dried and preheated with hot flue gas. The preheated coal is transferred to a rotating pyrolysis drum where it is heated to carbonization temperature by contact with hot ceramic balls. The balls are separated from the char and conveyed to a ball heater. The char produced is about 50 percent of the weight of the raw coal feed and contains about 80 percent of raw coal heating value. Economical use must obviously be found for this material. Pyrolysis vapors are cooled to condense oil and water from the gaseous products. The liquid products are fractionated into gas, oil, naphtha, and residuum. Gas is utilized in the ball heater as a fuel.

- Typical Products

Typical products obtained from Wyodak coal (a subbituminous coal from the Wyoming/Dakota region with a gross heating value of 8139 Btu per pound and 0.3 weight percent sulfur) are as follows:

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*The Oil Shale Corporation

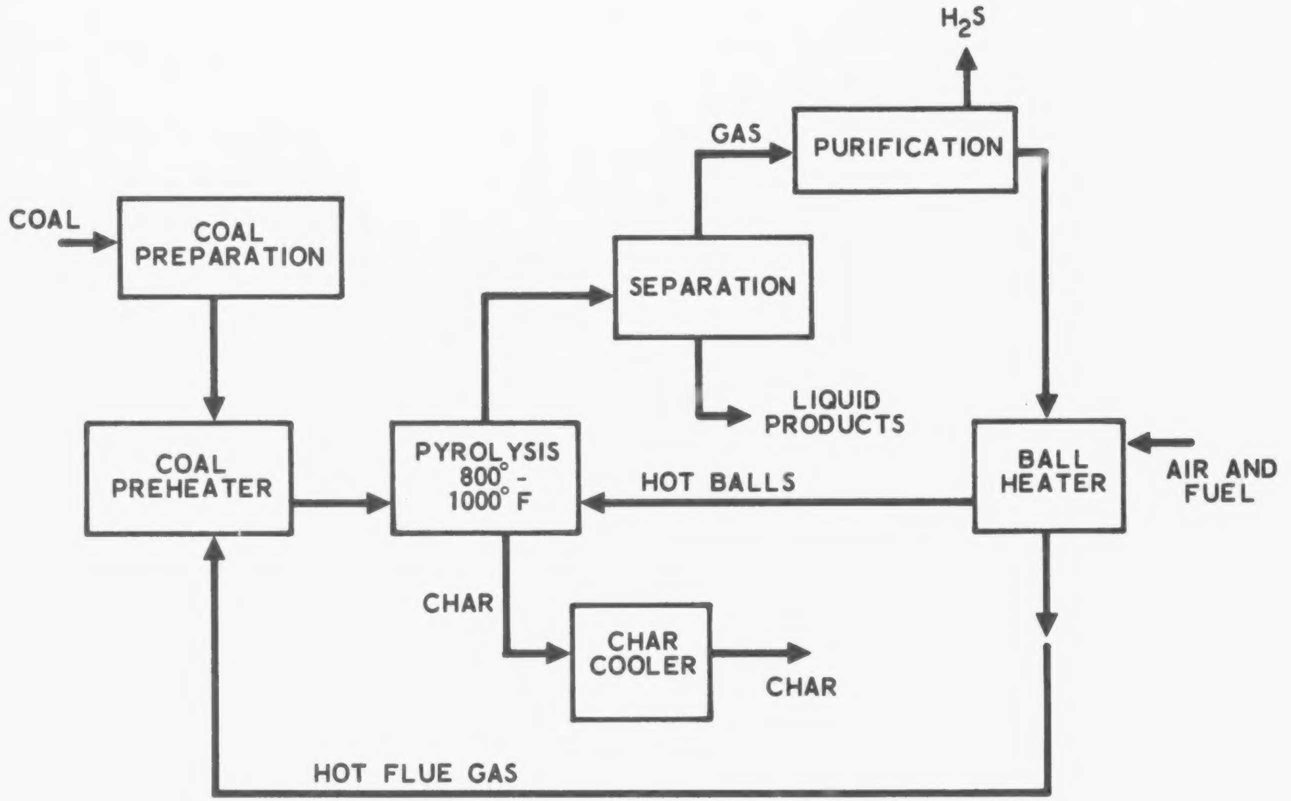
H$_2$S
GAS
PURIFICATION
COAL
COAL PREPARATION
SEPARATION
LIQUID PRODUCTS
COAL PREHEATER
PYROLYSIS 800° - 1000° F
HOT BALLS
BALL HEATER
AIR AND FUEL
CHAR
CHAR COOLER
CHAR
HOT FLUE GAS

Figure 3-2. TOSCOAL Process (Ref. 3-3)

Products	Product/Ton of Raw Coal 970°F	 800°F	Characteristics of Products
Gas, MSCF	1.625	0.438	600 (includes CO_2, H_2S) HHV Btu/SCF
Oil, barrels	0.52	0.25	6-13° API, HHV 16,000 Btu/lb
Char, pounds	970	1100	Sulfur 0.2-0.4%, 13,000 Btu/lb., 16%-25% volatiles

- Current Status

The Oil Shale Corporation has carbonized sub-bituminous coal in its 25 ton/day pilot plant located at Golden, Colorado.

Of the four principal processes based upon solvent separation or solvent extraction, two utilize direct hydrogenation of coal in the presence of an active catalyst followed by removal of mineral matter and unreacted coal. This is the concept employed in the SYNTHOIL and H-Coal processes described below.

3.1.3.3 SYNTHOIL Process Description

The SYNTHOIL Process (Figure 3-3) was developed by the Bureau of Mines to convert coal into fuel oil. Coal is crushed, dried, and slurried in a recycled portion of its own product oil. The slurry is fed to a fixed-bed catalytic reactor with turbulently flowing hydrogen. The combined effect of the hydrogen, turbulence, and catalyst is to liquefy and desulfurize the coal. A commercially available catalyst is used and consists of cobalt-molybdenum on silica activated alumina. The conditions of operation are 850°F and 2,000 to 4,000 psig. The violently moving slurry prevents plugging of the packed bed as the coal passes through its sticky plastic phase prior to becoming liquid; it also increases the mass transfer of hydrogen into slurry and keeps the catalyst surface clean by controlled attrition. The slurry residence time is less than 14 minutes, and reactor pressure drop is 150 psi. The product passes through a high-pressure receiver where the

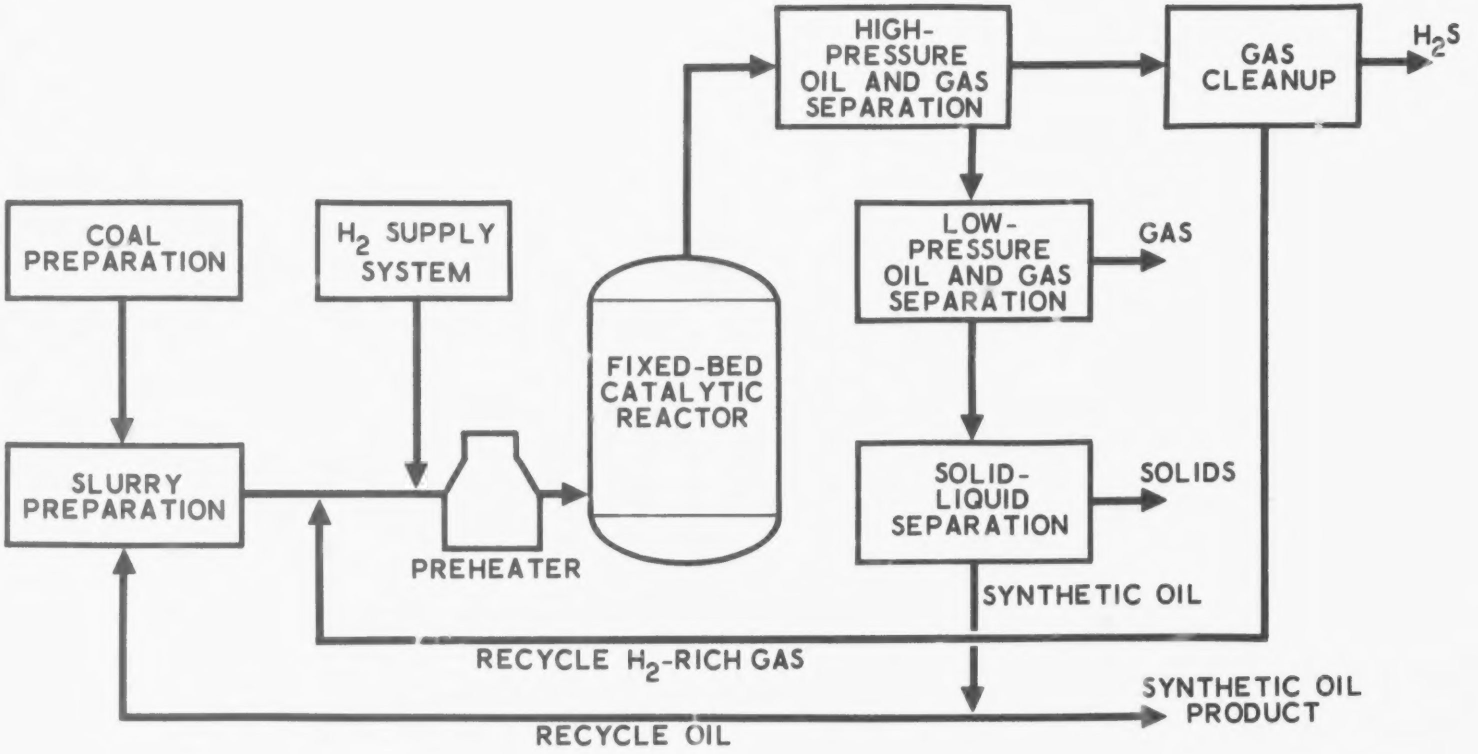
COAL PREPARATION
H_2 SUPPLY SYSTEM
SLURRY PREPARATION
PREHEATER
FIXED-BED CATALYTIC REACTOR
HIGH-PRESSURE OIL AND GAS SEPARATION
GAS CLEANUP
H_2S
LOW-PRESSURE OIL AND GAS SEPARATION
GAS
SOLID-LIQUID SEPARATION
SOLIDS
SYNTHETIC OIL
RECYCLE H_2-RICH GAS
SYNTHETIC OIL PRODUCT
RECYCLE OIL

Figure 3-3. SYNTHOIL Process (U.S. Bureau of Mines) (Ref. 3-3)

gas is separated and recycled after H_2S and NH_3 removal. The product slurry oil pressure is reduced in passing to a low-pressure receiver, and it is centrifuged to remove ash and organic coal residues. Part of the centrifuged oil is recycled as slurry oil and the remainder is the product oil.

- Typical Results - Treating Kentucky Coal

Hydrodesulfurization of Kentucky Coal

Experimental Conditions:

Liquid Feed Throughput: 140 lb/hr/ft^3 Reactor Volume
Slurry Feed: 45 Coal/55 Recycle Oil
Hydrogen Recycle Rate: 125 std. ft^3/hr
Pressure: 4,000 lb/in^2 gauge
Temperature: 450°C

Sulfur in Feed Coal, wt. %	4.6
Sulfur in Recycle Oil (Product Oil), Wt. %	0.19
Yield: bbl. oil/ton coal m.a.f.	3.0
Solvent Analysis of Product Oil, wt. %	
Oil (Pentane Soluble)	79.5
Asphaltene	17.4
Organic benzene insolubles	2.1
Ash	1.0
Elemental Analysis of Product Oil (Ash-Free), wt. %	
Carbon	89.9
Hydrogen	9.2
Nitrogen	0.19
Viscosity of Product Oil, SSF at 180°F	21-30
Calorific Value of Product Oil, Btu/lb	17,700

- Current Status

The SYNTHOIL process is being tested in a small 5 to 10-pounds-per-hour pilot plant. A pilot plant capable of processing 1/2 tons of coal per day, with output of 1.5 barrels per day of oil has been started up in Bruceton, Pennsylvania, and plans are being formulated for construction of an 8-ton-per-day pilot unit.

3.1.3.4 H-Coal Process Description

The H-Coal process can produce synthetic crude oil from coal (Figure 3-4). Coal is dried, pulverized (minus 40 mesh), and slurried with coal-derived oil. The slurry, mixed with hydrogen, is preheated and fed to

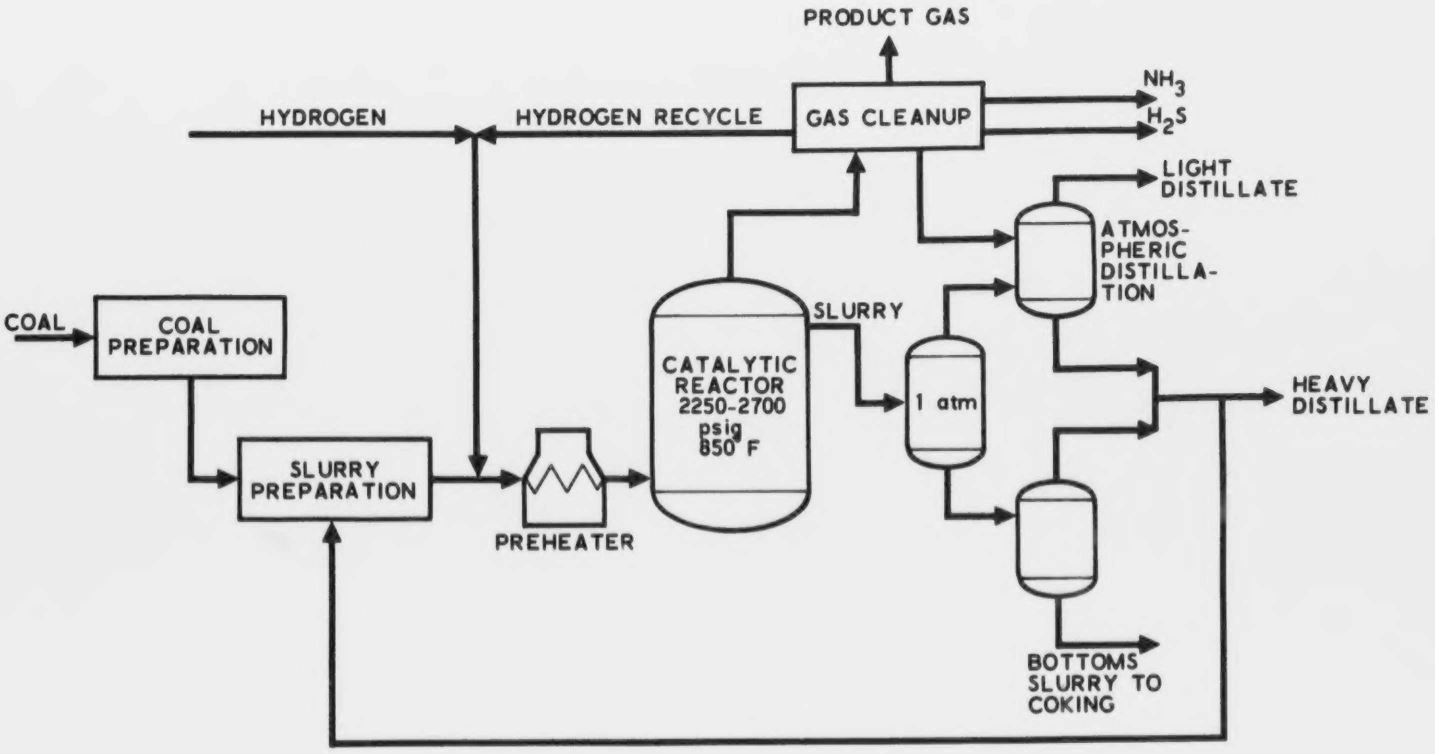
PRODUCT GAS
HYDROGEN
HYDROGEN RECYCLE
GAS CLEANUP
NH_3
H_2S
LIGHT DISTILLATE
ATMOSPHERIC DISTILLATION
COAL
COAL PREPARATION
SLURRY
CATALYTIC REACTOR 2250-2700 psig 850 F
1 atm
HEAVY DISTILLATE
SLURRY PREPARATION
PREHEATER
BOTTOMS SLURRY TO COKING

Figure 3-4. H-Coal Process (Hydrocarbon Research, Inc.) (Ref. 3-3)

an ebullating bed reactor containing a cobalt-molybdenum catalyst. The coal is hydrogenated and converted to liquid and gaseous products. Reactor conditions are about 850°F and 2700 psig. A constant catalyst activity is maintained by adding and withdrawing catalyst continuously. A slurry of unconverted coal and liquid product is let down from the reactor to an atmospheric-pressure flash drum. Flash vapors go to an atmospheric distillation tower and the bottom products are further processed in a vacuum tower to obtain vacuum distillate overhead and a vacuum bottoms slurry product. The light hydrocarbon vapors in the gas leaving the reactor are removed in a recycle gas scrubber. Ammonia and hydrogen sulfide are removed and gas is recycled to the H-Coal reactor. A part of the heavy distillate product from the top of the vacuum distillation and the bottom of the atmospheric distillation are recycled as slurry oil.

- Typical Products

Typical products from Illinois No. 6 bituminous coal are as follows:

IBP Cuts	Volume, %	Gravity, °API
IBP - 400°F	42.18	44.6
400 - 650°F	41.51	17.3
650 - 975°F	16.31	5.0

- Current Status

This process has been operated on a 3-ton-per-day pilot plant scale.

An alternate approach has also been developed in which the first stage consists of mild hydrogenation without a catalyst. After solids rejection, the extract (or solvent refined coal) is further processed over a catalyst if the end products so dictate. This is the route followed by Pittsburgh & Midway Coal Mining Company (a subsidiary of Gulf Oil Corporation) in the Solvent Refined Coal (SRC) process and by the Consolidation

Coal Company in the Consol Synthetic Fuel (CFS) process. In the former case, gaseous hydrogen at elevated pressure is used in the extraction step while a donor solvent supplies the hydrogen in the CSF process. Both concepts are reviewed in the following pages.

3.1.3.5 SRC Process Description

The Solvent Refined Coal (SRC) process produces a low-sulfur, ash-free material that can be handled in either a liquid or solid form (Figure 3-5). Coal is ground to minus 200 mesh size, dried, and mixed with a coal-derived solvent having a boiling range of 500° to 800°F. The slurry, together with hydrogen, is heated to 815°F at 1,000 psi causing complete solution of the organic matter. Hydrogen requirement varies from 15,000 to 80,000 SCF/ton of coal. Gas from the dissolver is separated in a high-pressure, flash vessel operating at 995 psia and 625°F. Liquid and solids from the flash vessel go to a rotary filter where undissolved coal solids are removed. The filtrate is sent to a vacuum distillation. The overhead fraction is solvent for recycle and product light oil. The bottom fraction is a hot liquid with a solidification point of about 300°F (solvent refined coal), having a heating value of about 16,000 Btu/pound. Gas from the high-pressure flash tank is treated for acid-gas removal before recycling it to the dissolver. In this process all the pyritic sulfur and over 60 percent of the organic sulfur, and most of the ash are removed from the coal. Solids from the filtration system are dried to recover solvent. The dried solids containing about 35 to 55 percent by weight undissolved carbon and about 5 to 8 percent sulfur are burned in a fluidized combustor to generate steam. Stack gas containing SO_2 reacts with H_2S from the gas scrubbing system in a Claus plant to produce sulfur. The liquid product can be transported hot as a liquid fuel or can be allowed to cool below 300°F to solidify and produce a relatively clean solid fuel.

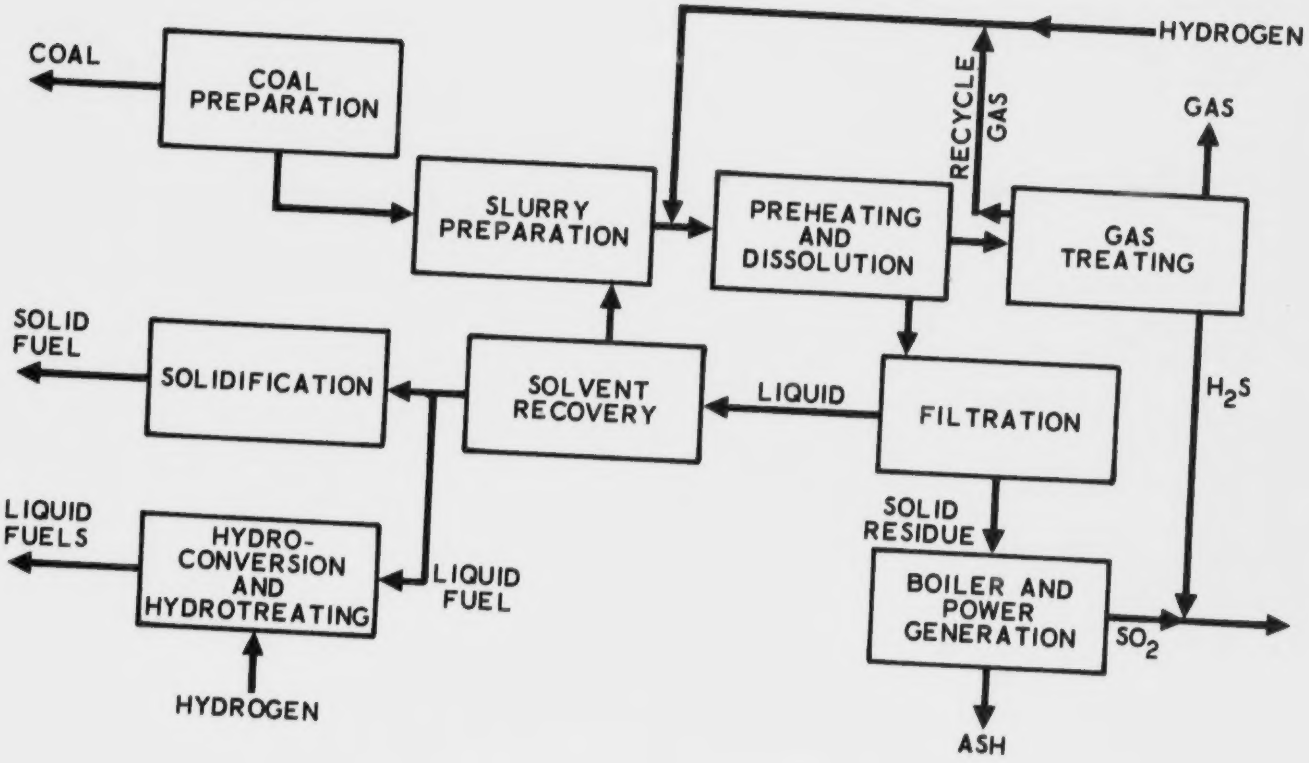
COAL
COAL PREPARATION
SLURRY PREPARATION
PREHEATING AND DISSOLUTION
GAS TREATING
HYDROGEN
RECYCLE GAS
GAS
SOLID FUEL
SOLIDIFICATION
SOLVENT RECOVERY
LIQUID
FILTRATION
H2S
LIQUID FUELS
HYDRO-CONVERSION AND HYDROTREATING
LIQUID FUEL
HYDROGEN
SOLID RESIDUE
BOILER AND POWER GENERATION
SO2
ASH

Figure 3-5. Solvent Refined Coal Process (The Pittsburgh & Midway Coal Mining Company) (Ref. 3-3)

- Typical Products

	Raw Coal	Wt. %	Product Solvent Refined Coal
Carbon	70.7		88.2
Hydrogen	4.7		5.2
Nitrogen	1.1		1.5
Sulfur	3.4		1.2
Oxygen	10.3		3.4
Ash	7.1		0.5
Moisture	2.7		---
	100.0		100.0
Volatile matter	38.7		36.5
Fixed Carbon	51.5		63.0
Ash	7.1		0.5
Moisture	2.7		---
	100.0		100.0
Btu/lb	12,821		15,768

- Current Status

Construction of a 50-tons/day plant is under way in Fort Lewis, near Tacoma, Washington. Completion was scheduled for late 1973. A pilot plant is also located in Wilsonville, Alabama. These plants produce a solid fuel product.

3.1.3.6 Consol Process Description

The Consol Synthetic Fuel Process (Figure 3-6) can produce liquid hydrocarbon fuel from coal. Crushed coal (minus 14 mesh), is dried and preheated in a fluid bed to 450°F. It is then slurried with a coal derived solvent and pumped at 150 psig through a tubular furnace where it is heated to an extraction temperature of 765°F. Extraction occurs mainly in a stirred extraction vessel. Vapors produced in the extraction section are sent to the solvent recovery section. Unreacted coal and liquid product are separated in hydroclones. Liquid passes to the solvent recovery section, and solids are sent to a low-temperature carbonization unit.

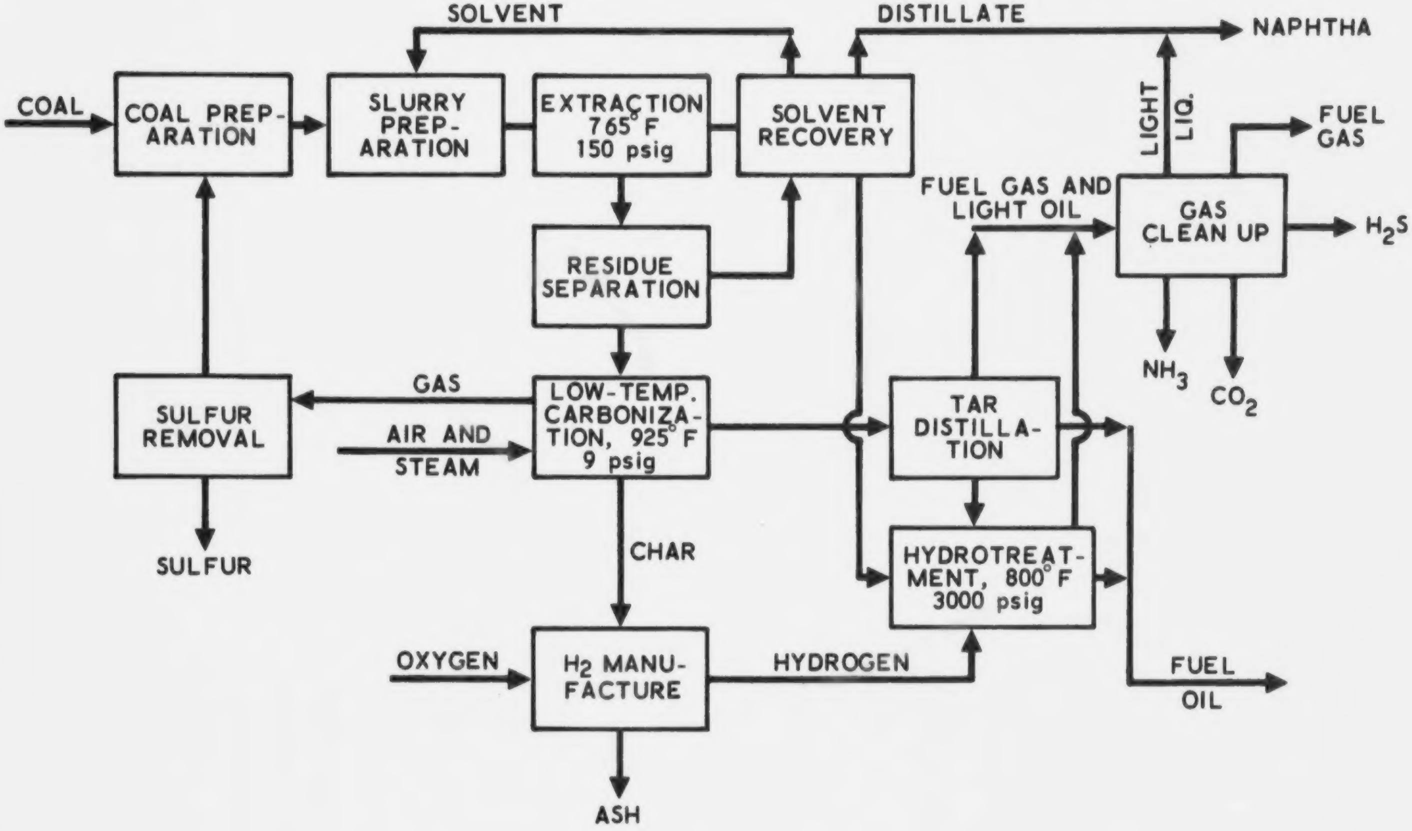
SOLVENT
DISTILLATE
NAPHTHA
COAL
COAL PREPARATION
SLURRY PREPARATION
EXTRACTION 765° F 150 psig
SOLVENT RECOVERY
LIGHT LIQ.
FUEL GAS
FUEL GAS AND LIGHT OIL
GAS CLEAN UP
H2S
RESIDUE SEPARATION
NH3
CO2
GAS
SULFUR REMOVAL
AIR AND STEAM
LOW-TEMP. CARBONIZATION, 925° F 9 psig
TAR DISTILLATION
SULFUR
CHAR
HYDROTREATMENT, 800° F 3000 psig
OXYGEN
H2 MANUFACTURE
HYDROGEN
FUEL OIL
ASH

Figure 3-6. Consol Synthetic Fuel (CSF) Process (Consolidation Coal Company) (Ref. 3-3)

Solvent for recycle to the extraction process is distilled from the liquid. The remaining liquid, along with tars from the carbonization unit, is treated with hydrogen in a reactor system operating at 800°F and 3000 psi and using a cobalt-moly-nickel catalyst. This desulfurizes and upgrades the product fuel oil. Hydrogen for this operation is produced from the char of the carbonization unit.

Gas streams from the carbonization and hydrotreating operations are treated for removal of H_2S, NH_3, CO_2 and light hydrocarbon liquids. This produces a clean fuel gas and a naphtha liquid product.

- Typical Products Using Pittsburgh Seam Coal (Ireland Mine)

Product	Product/Ton of Raw Coal	Characteristics of Products
Gas	3.424 MSCF	HHV 933 Btu/SCF
Naphtha	0.52 bbl	58° API, 5.2 MMBtu/bbl, 0.056 Wt%S
Fuel Oil	1.52 bbl	10.3° API, 6.3 MMBtu/bbl, 0.128 Wt%S
Ammonia	11.00 lb	
Sulfur	71.00 lb	
Ash	213.60 lb	

- Current Status

A 70-ton per day pilot plant was operational at Cresap, West Virginia for 40 months with less than 500 hours of operating time. It was shut down in April 1970 for a detailed study of the process and its operating problems. The original intent was to make liquids in the gasoline range; but, if the plant were to be reactivated, it would be modified to maximize production of low-sulfur fuel oil.

All the foregoing processes provide a synthetic crude oil of varying composition suitable for processing in a conventional petroleum refinery. The refinery processes will not be reviewed here, since they are standard methods described in any text on petroleum refining. However, the processing sequence will probably differ from that used for petroleum-derived crudes because of differences in chemical and physical properties.

3.1.3.7 Oil Shale

Thus far in this section, the topic has been the liquefaction of coal. We turn now to the recovery of oil from oil shale deposits in the Western United States. Oil shale is a finely textured sedimentary rock containing the solid, largely insoluble organic material, kerogen. High temperature decomposes the kerogen, yielding a viscous oil which can be upgraded to a product suitable for use as a refinery feedstock. There are two principal routes to recovering the oil contained in shale: conventional, above-ground retorting of mined shale and in-situ retorting. Each approach involves several stages that have been developed to various degrees, as summarized in Figure 3-7. Above-ground retorting is almost ready for commercialization, while in-situ recovery is still in the exploratory stage.

The two methods of recovery are complementary rather than competitive. Where the shale can be mined inexpensively, such as where relatively rich shale crops out or where the overburden is shallow, above-ground processing will probably be used. However, where the shale is deeply buried and in varying layers of rich and lean shale, in-situ processing would be advantageous.

This discussion of shale oil recovery processes will be confined to above-ground retorting, which is the more advanced approach, although in-situ recovery has many attractive features if developed, primarily elimination of spent shale disposal. The principal efforts in developing oil shale retorts have been made by the Bureau of Mines, Union Oil Company, and The Oil Shale Corporation.

In the BuMines Combustion Process, crushed shale (1/4 to 2 inches) is fed to the top of a cylindrical retort and falls successively through preheating, retorting, combustion, and cooling zones to a grate and lock

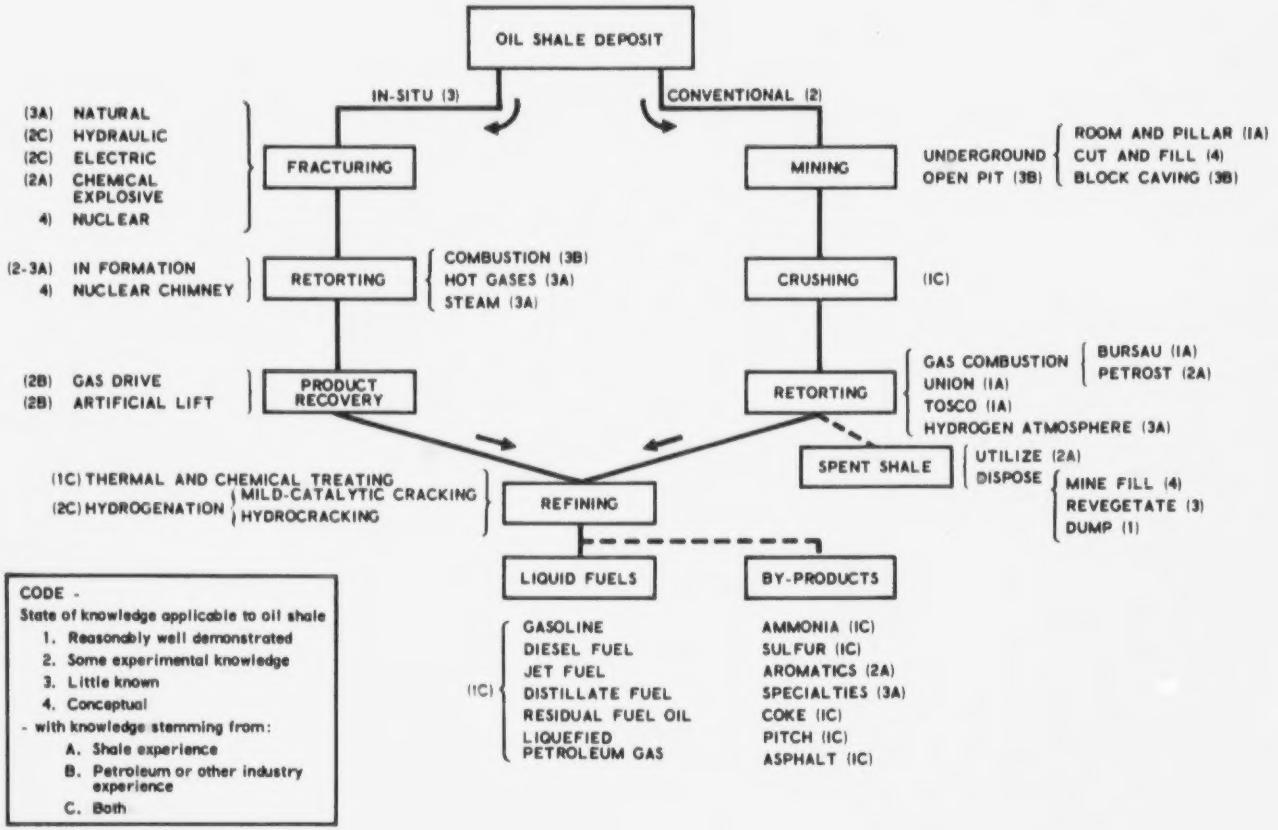
OIL SHALE DEPOSIT
IN-SITU (3)
CONVENTIONAL (2)
(3A) NATURAL
(2C) HYDRAULIC
(2C) ELECTRIC
(2A) CHEMICAL EXPLOSIVE
4) NUCLEAR
FRACTURING
MINING
UNDERGROUND
OPEN PIT (3B)
ROOM AND PILLAR (IA)
CUT AND FILL (4)
BLOCK CAVING (3B)
(2-3A) IN FORMATION
4) NUCLEAR CHIMNEY
RETORTING
COMBUSTION (3B)
HOT GASES (3A)
STEAM (3A)
CRUSHING
(IC)
(2B) GAS DRIVE
(2B) ARTIFICIAL LIFT
PRODUCT RECOVERY
RETORTING
GAS COMBUSTION
BURSAU (IA)
PETROST (2A)
UNION (IA)
TOSCO (IA)
HYDROGEN ATMOSPHERE (3A)
SPENT SHALE
UTILIZE (2A)
DISPOSE
MINE FILL (4)
REVEGETATE (3)
DUMP (1)
(1C) THERMAL AND CHEMICAL TREATING
(2C) HYDROGENATION
MILD-CATALYTIC CRACKING
HYDROCRACKING
REFINING
LIQUID FUELS
BY-PRODUCTS
(IC)
GASOLINE
DIESEL FUEL
JET FUEL
DISTILLATE FUEL
RESIDUAL FUEL OIL
LIQUEFIED PETROLEUM GAS
AMMONIA (IC)
SULFUR (IC)
AROMATICS (2A)
SPECIALTIES (3A)
COKE (IC)
PITCH (IC)
ASPHALT (IC)
CODE -
State of knowledge applicable to oil shale
1. Reasonably well demonstrated
2. Some experimental knowledge
3. Little known
4. Conceptual
- with knowledge stemming from:
A. Shale experience
B. Petroleum or other industry experience
C. Both

Figure 3-7. Oil-Shale Utilization - Routes and State of Knowledge (U.S. Department of the Interior, 1968) Ref. 3-5

hopper. Recycle gas, mostly inert but containing a small amount of hydrocarbon vapor, flows up from the bottom. Air is introduced through nozzles above the cooling zone, burning the residual carbon off the shale, producing a temperature of 1,600 to 1,800°F in the gas and on the lump surfaces, and decomposing about one quarter of the shale carbonate. In the retorting zone where the kerogen decomposes, the temperature is 800 to 900°F. Flow of the gases upward through the fresh downcoming shale to the peripheral top outlet ports cools the gas to 130°F and forms a suspended oil mist which passes through centrifugal separators and an electrostatic precipitator, yielding a crude oil of 20° API gravity and 80°F pour point and a gas which is split into two streams; part being recycled to the retort and part going to a steam plant. The retorting efficiency is 90 percent (the percent of that oil yield obtainable in a standard Fischer Assay of the feed). The process has been demonstrated on a 260-ton-per-day scale by the Colorado School of Mines Research Institute.

In the Union Oil process, shale is charged into the lower and smaller end of a vertical truncated cone and is pushed upward against downflowing process gas. One retort in four uses air for partial combustion of the carbon residue in the shale (maximum temperature 2,200°F); its product gas, after separation from the oil, is burned to preheat the rich nitrogen-free recycle gas from the other three retorts. The preheated recycle gas is fed to the top of all four retorts, producing a maximum temperature of 950°F in the three unfired retorts. The process has the advantages over the BuMines process of not dripping oil products into hotter parts of the charge for recracking and of permitting an improved thermal balance by proper portioning of the recycle gas. The average retort efficiency (Fischer Assay) is 91 percent. The process was demonstrated at a rate of 1,000 tons shale/day in 1958.

The TOSCO II retorting process uses hot ceramic balls to heat the shale in a horizontal rotating kiln to 920°F (Figure 3-8). The balls are separated from the spent shale, reheated in a furnace fired with product

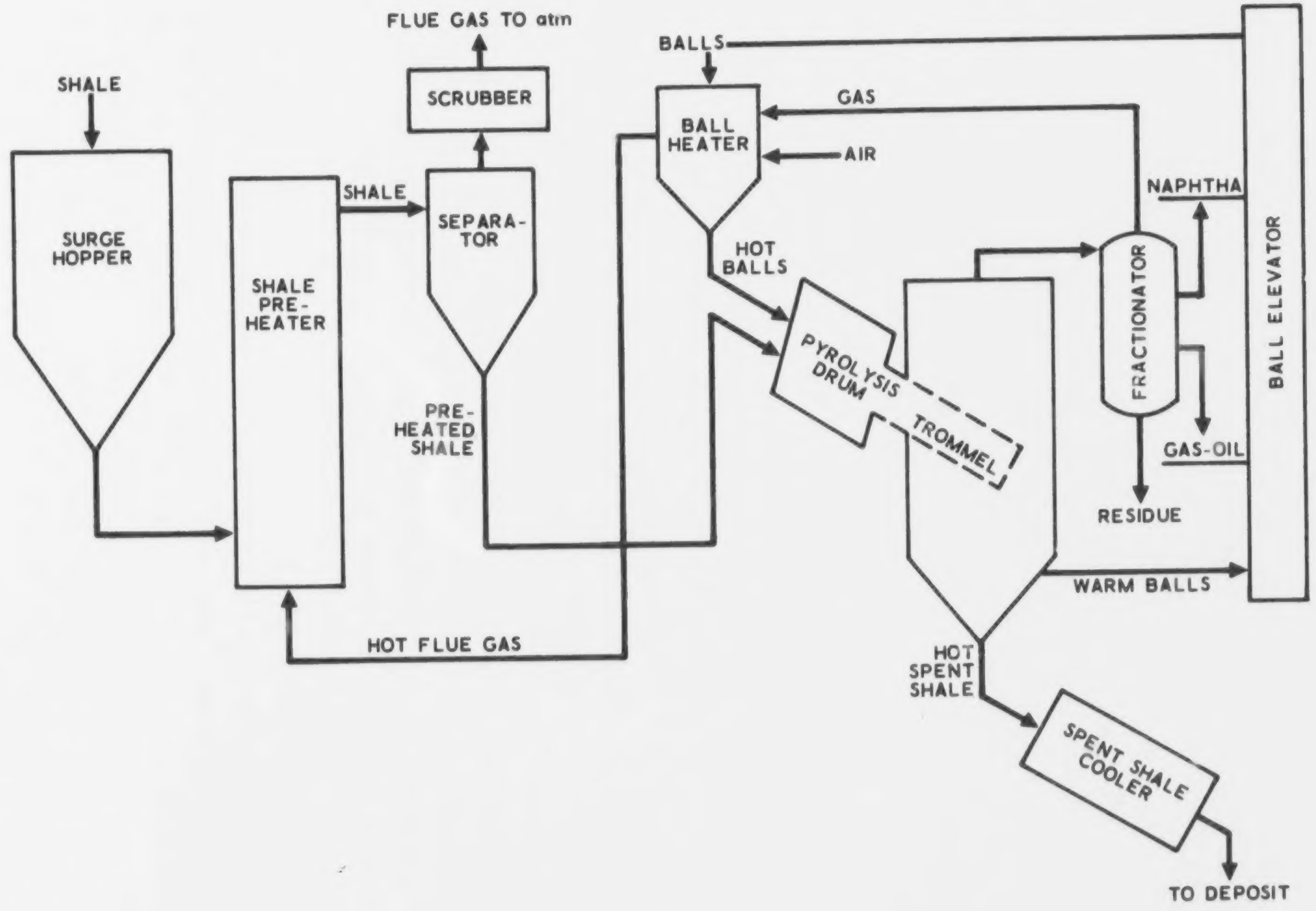
FLUE GAS TO atm
SHALE
SCRUBBER
BALLS
GAS
BALL HEATER
AIR
SURGE HOPPER
SHALE
SEPARA-TOR
SHALE PRE-HEATER
NAPHTHA
HOT BALLS
FRACTIONATOR
BALL ELEVATOR
PYROLYSIS DRUM
TROMMEL
PRE-HEATED SHALE
GAS-OIL
RESIDUE
WARM BALLS
HOT FLUE GAS
HOT SPENT SHALE
SPENT SHALE COOLER
TO DEPOSIT

Figure 3-8. TOSCO Process for Oil Shale Treatment (Ref. 3-5)

gas, and returned to the retort. Flue gas from the ball furnace is used to preheat the shale. The retort efficiency, based on standard Fischer Assay, is 105 percent. The process was demonstrated at a rate of 1, 000 tons of shale per day in 1967.

The product of any of the retorting processes is too viscous for piping to a refinery. The upgrading process starts with a 650°F flash over into 40 percent overhead and 60 percent residuum; the latter is heated to 900°F and sent to coke drums. Gas oil and naphtha streams are separately hydrofined in multiple-bed reactors consuming 2, 100 and 1, 500 SCF, respectively, of 97 percent H_2 per barrel of charge. The final byproducts, based on 50, 000 bbl/SD* of 43° API syncrude, are 820 T/SD** of coke, 162 T/SD of ammonia, and 66 T/SD of sulfur. This is a rather severe upgrading process, producing an excellent refinery feedstock. However, large water requirements may prevent such processing in arid shale regions. The alternative is a relatively low water requirement, mild heat treatment to reduce viscosity ("visbreaking") which will allow pipeline transport of the crude to the refinery.

3.1.4 Physical and Chemical Properties

A compilation of property data for the liquid hydrocarbon fuels is given in Table 3-2. Note that the data are for petroleum-derived products. There are several reasons for this situation. Relatively little data are available on many properties of refined coal and shal liquids. What has been published may not be representative of the products that finally are commercially produced. Indeed, it is probable that at least some refined fractions, such as gasoline, will be made from blends of petroleum- and synthetic-derived material. Other than some increase in the aromatic content of coal-derived products, it appears that the liquid hydrocarbon fuels made in whole or part from synthetic crude will be similar to present petroleum fuels when sold to the consumer.

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*Barrels per stream day

**Tons per stream day

Table 3-2. Properties of Conventional Hydrocarbon Liquid Fuels[a]

	Gasoline	Naphtha	Kerosene	Diesel Oil and No. 2 Fuel Oil
Elementa Composition	C 84.90% by wt H_2 15.02% S 0.08%	C 84.7% by wt H 15.3%	C 84% by wt H 16% by wt	C 85 H 14 S 1%
Boiling Point, °F	89 - 406	95 to 450	300 - 480	380 - 650
Density, Liquid, lb/ft^3	45.5	48	50.6	53.4
Specific Gravity, Liquid	0.7275	0.77	0.811	0.856
Heating Value Liquid				
Volumetric Gross, B/ft^3	941,850	974,400	1,012,000	1,046,301
Volumetric Net, B/ft^3	877,740	905,472	941,160	987,017
Weight Gross, B/lb	20,700	20,300	20,000	19,590
Weight Net, B/lb	19,290	18,864	18,600	18,480
Air for Combustion - Liquid				
O_2 Weight, lbs/lb	3.455	3.470	3.455	3.281
N_2 Weight, lbs/lb	11.49	11.547	11.495	10.919
Air Weight, lbs/lb	14.945	15.017	14.950	14.200
Products of Combustion - Liquid				
CO_2 Weight, lbs/lb	3.004	3.103	3.114	3.218
H_2O Weight, lbs/lb	1.342	1.367	1.341	1.057
N_2 Weight, lbs/lb	11.494	11.547	11.495	11.019
Flame Velocity, ft/sec	1.4	1.10	–	–
Ignition Temperature, °F	536 to 804	450 to 530	490	490
Research Octane No.	92 - 100	30 to 50	30 - 50	30 - 50
Cetane No.	18	NA[b]	56 - 40	56-40

[a] Property data are for petroleum-derived products. Fuels from oil shale are expected to be similar. Coal-derived fuels may show some differences due to higher aromatic content.

[b] Not available, estimated to be between 18 and 40.

3.2 SUITABILITY FOR USE AS AN ENGINE FUEL

Little information is available on the use of synthetic gasoline or distillates in automotive engines. In the post-World War II period, the Bureau of Mines produced some motor gasoline from the liquid phase catalytic hydrogenation of sub-bituminous coal. There were no obvious product quality problems; in fact, the gasoline was successfully field-tested in Army vehicles under sustained high load conditions. The Navy successfully tested, in sea trials, a boiler fuel produced from coal via the FMC Corp. COED process in late 1973. With regard to shale oil, a diesel oil prepared from this source was used in the 1950s to fuel a locomotive operating between Denver and Salt Lake City. (Ref. 3-6)

On the basis of the limited information cited above, it is evident that there is need for a test program to investigate the compatibility of these coal and shale derived synthetic fuels with automotive engines. Such an effort is planned for FY 1975 under an interagency agreement between EPA and the Bureau of Mines. An experimental effort by the Bureau of Mines will investigate the combustion characteristics of synthetic fuels followed by field tests to reveal the feasibility and limitations of these fuels in the operating environment of current road vehicles.

A qualitative assessment of the synthetic fuels' compatibility with four classes of engines is shown in Table 3-3. The estimates are based upon the fact that shale-derived transportation fuels will probably be almost indistinguishable from conventional petroleum fuels, while coal-derived fuels will have a much higher aromatic content. In the case of blended petroleum-synthetic fuels, of course, any differences in properties will be mitigated. As indicated in the table, the synthetic fuels would be expected to have about the same compatibility characteristics as their petroleum analogues.

Table 3-3. Fuel/Engine Compatibility (Ref. 3-7)

Engine Class Characteristics	Car Compatibility Rating[a] With Indicated Engine Class[c]			
F/A Conditions → Combustion → Ignition →	Homo. Intermit. Spark	Hetero Intermit. Sp, GP, PI[b]	Hetero Intermit. Comp.	Hetero Continuous NA
Fuel↓				
Pet. Gasoline	4	4	2e	4
Pet. Distillate	1d	2f	4	4
Shale - Gasoline	4	4	2e	4
Shale - Distillate	1d	2f	4	4
Coal - Gasoline	4gh	4h	2eh	3hj
Coal - Distillate	1d	2fh	3i	3hj

Footnotes:

a Compatibility Rating

4	No car modifications required
3	Minor modifications required
2	Major modifications required
1	Not practical

Letters indicate modifications required as described below.

b Types of Ignition

Sp - Spark
GP - Glow Plug
PI - Pilot Injection

c Engines in the Various Classes

Class			
A/F	Combust.	Ignition	Engine Types
Homo.	Intermit.	Spark	Otto Cycle; reciprocating and rotary
Hetero.	Intermit.	Spark, etc.	Stratified charge; recip. and rotary
Hetero.	Intermit.	Compression	Diesel Cycle; recip. and rotary
Hetero,	Continuous	--	Gas Turbine, Stirling, Rankine

Modifications Required Relative to Current Engines

d Octane number and volatility too low

e Will require very high compression ratio (~22) for satisfactory ignition (current compression ratio ~15)

f Pilot injection requires a secondary fuel & injection system; Spark requires installation of electric system plus distributor; Glow Plug requires installation of electric resistor in combustion chamber and necessary ancillary electric rig.

g Change carburetor jets

h May need some changes in gaskets, diaphragms, hose or other elastomeric parts in fuel system

i Low cetane number may require special starting technique

j May require modification in combustor design, for better cooling, cleaner combustion, reduction in smoke

3.2.1 Fuel Economy Effects

In general, fuel economy for these liquid hydrocarbon fuels will be more a function of the thermal efficiency differences between engine types than between fuels. However, there is some variation in heat content for these fuels, as can be noted from the data in Table 3-2. Generally, the heating value on a weight basis increases as the specific gravity decreases. Thus, gasoline with a specific gravity of 0.73 contains 19,290 Btu/lb while No. 2 fuel oil with a specific gravity of 0.86 contains 18,480 Btu/lb. Conversely, the volumetric heat content varies directly with specific gravity. The preceding numbers are pertinent to petroleum-derived fuels. The trend to higher aromatic content for coal liquids and shale liquids will provide a lower heating value on a weight basis but higher volumetric values.

3.2.2 Emission Effects

Emission data are not yet available for synthetic hydrocarbon fuels in current or advanced automotive engines. There is a definite need for such test data despite the general similarity of the synthetic fuels to their petroleum derived counterparts. A first step in obtaining such information is a planned interagency agreement between EPA and the Bureau of Mines which established a program for an engine combustion investigation with gasoline and diesel fuel derived from coal and shale, as well as fuel blends with petroleum-derived fuels. The program is expected to be completed during FY 1975. Physical, combustion, and emission characteristics are to be determined in engine dynamometer tests in order to reveal the feasibility and limitations in the use of synthetic fuels in contemporary automobile engines. Follow-on work of a similar nature will be necessary to evaluate the synthetic hydrocarbon fuels in advanced engines; e.g., Rankine and Brayton cycle external combustors.

3.2.3 Toxicity Effects

The following paragraphs are general discussions of health hazards involved in handling these fuels.

3.2.3.1 Gasolines from Coal or Shale

These gasolines would be expected to contain the same range of hydrocarbon types as petroleum derived gasolines. However, the concentration of aromatic hydrocarbons in the coal-derived fuels is expected to be relatively high. Experience has shown that gasoline of considerable difference in compositions have the same general toxicological properties.

- Toxicity. Gasolines generally act as irritants to skin and mucous membrane and as anesthetics resulting from depression of the central nervous system. Mucous membrane (eye, nose, throat) irritation may be produced by vapor or liquid. Skin contact is irritating. On a prolonged or repeated basis this contact may produce defatting of the skin leading to dermatitis. Gasoline from coal, particularly, should be evaluated for carcinogenic properties.

  The oral toxicity of gasoline is low; however, the aspiration effects are significant. Minute amounts of liquid gasoline which may be drawn into the lungs can be rapidly fatal.

  The dermal toxicity of gasoline is low. It is doubtful that toxicologically significant amounts can be absorbed through the skin.

  The most important route of entry of gasoline is by inhalation. Excessive exposure to gasoline vapors may induce symptoms of alcoholic intoxication including a feeling of fullness in the head, headache, blurred vision, dizziness, unsteadiness, nausea, and allied symptoms. The time of onset and the severity of these signs and symptoms is inversely related to the concentration. The olefin and aromatic content of the gasoline is important as these materials are more potent anesthetics. The irritant properties of the vapor cannot always be relied upon to provide an adequate warning.

The question of effects from long-term exposure to low level of petroleum-derived gasolines is controversial. Vague and ill-defined effects have been suggested, but no well-documented cases exist. The amount of benzene present in any gasoline assumes importance where prolonged or repeated low level exposure is possible. Benzene causes the destruction of the blood-forming organs leading to aplastic anemia and has been implicated in certain cases of leukemia. No reports have been made of such effects from benzene-containing gasolines, but the exact exposure levels are not known.

- Hazard.
  - Oral ingestion. low apart from risk of aspiration
  - Skin penetration. low
  - Vapor inhalation. high, particularly in confined space where vapor concentrations can build up rapidly
  - Skin, eye, nose, and throat contact. moderate risk of irritancy.

3.2.3.2 Distillates from Coal or Shale

These distillates would be expected to contain the same range of hydrocarbon types as petroleum distillates in the 380° to 650°F boiling range.

- Toxicity. Distillates generally act as irritants to skin and mucous membranes. Toxicity is low by the oral, dermal, and vapor inhalation routes. However, aspiration, the entry of small amounts of liquid hydrocarbon directly into the lungs, rapidly produces severe injury to lung tissues which may be fatal. The low volatility of distillates precludes vapor build-up unless the liquid has been heated.

Skin contact may be irritating and on a prolonged bases can remove sufficient fat from the skin to result in a dermatitis. Distillate from coal, particularly, should be evaluated for carcinogenic properties. Eye contact results in only slight, transient irritation.

- Hazard
  - Oral ingestion. low apart from risk of aspiration which is very hazardous
  - Skin penetration. low
  - Vapor inhalation. low
  - Skin, eye, nose, and throat contact. low risk of irritancy, increasing with increased severity of exposure.

3.2.4 Safety Effects

Only a few general comments need be made since these fuels are in general use now, and the safety effects of coal or shale-derived material should be similar to those of current fuels. Fire and explosion are the principal hazards, particularly for the lower boiling fractions such as gasoline. Higher boiling fuels, such as diesel and fuel oils, present only a fire hazard due to their low volatility.

3.2.5 Handling, Storage, and Distribution Requirements

As for the two preceding topics, the current widespread use of these hydrocarbons obviates the need for an extended discussion of handling, storage and distribution requirements. In fact, it is particularly these factors that make such fuels so attractive as alternatives to their petroleum-derived counterparts.

3.2.6 Critical Research Gaps

From an overall standpoint, the most important technical gap is in the production processes for obtaining these fuels from coal or shale. To date, the preponderance of federal R&D funding in the fuel-from-coal area has been for gas production, although there are recent indications that there will be some shift toward support of coal liquefaction technology. In the engine performance and emissions area there is essentially no experience in automotive usage for these synthetic fuels. The Bureau of Mines synthetic fuels evaluation program, planned for FY 1975, should furnish valuable data on engine compatibility and exhaust emissions, at least for current road vehicles.

3.3 CURRENT STATUS

There is no current commercial production of liquid fuels from coal or shale in the United States although a number of pilot plants have been built and operated. The problem of coal liquefaction differs from that of gasification because an acceptable technology for liquefaction has yet to be proven (Ref 3-8). The buildup rate of a synthetic-liquid enterprise in the United States is therefore dependent, among other factors, on the rate at which technology is developed. The technical situation for shale extraction is somewhat better with at least one retorting process available for near-term commercial scaleup. The forecasted production schedule and limiting factors are discussed in detail in Section 3.4.

3.4 PROJECTED STATUS

3.4.1 Availability

With regard to shale oil, many uncertainties make it difficult to predict production levels through the rest of the century. On the one hand, the resource base is extensive, the cost of production is moderate, and the technology is fairly well developed. On the other hand, there are very significant environmental problems: federal leases must be made available in adequate number and economic size, and the capital-intensive mining and retorting must be carried out in remote locations.

The National Petroleum Council forecast (Ref. 3-8) was published in December 1972, prior to the Arab oil embargo, the declaration of "Project Independence", and the probable congressional funding of substantial, energy-related R&D. In this document, the maximum shale oil production rate on a non-emergency basis was forecast to reach 750 Mbbl/day* in 1985. An intermediate rate would be 400 Mbbl/day. Detailed forecasts were not made beyond 1985.

A more recent appraisal of the projected capacity and production buildup of shale oil was made by Esso Research and Engineering Company** (Ref. 3-6). Their preliminary schedule is shown in Table 3-4. Production increases from 400 Mbbl/day in 1985 to 900 Mbbl/day in 1990 and to 3,200 Mbbl/day in 2000, corresponding to a 15 percent/year growth rate. A growth rate of that magnitude over that time span is possible but uncommon, as an example, for tonnage petrochemicals. The forecast also makes the very important assumption that in-situ recovery methods will become available in the 1985 to 1990 period. As stated, these projections indicate that shale oil cannot meet the total expected transportation fuel demand and that conventional petroleum or other synthetic fuels would also be needed.

Reference 3-8 also presents several rates for coal-derived liquid fuel production buildup. For the intermediate supply case, the first commercial plant of 30 Mbbl/day would come on stream in 11 years (1985) with a second plant of 50 Mbbl/day added about 4 years later. A faster buildup is also visualized under greater economic incentives or new government policies but still limited by technology growth. This maximum case predicts 1984 production at 200 MB/day, reaching 680 Mbbl/day by 1987.

The initial coal-derived liquid fuel forecast by Exxon (Ref. 3-6) is shown in Table 3-5. They postulate 100 Mbbl/day liquid production by 1982, growing to 900 Mbbl/day by 1990, to 2700 Mbbl/day by 2000. This represents

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*Mbbl/day - thousands of barrels per day

**Currently Exxon Research and Engineering Company

Table 3-4. Plausible Schedule for Buildup of Shale Oil Capacity and Production (Ref. 3-6)

Year	Nominal Capacity, Mbbl/day at Year End	Average Production, Mbbl/Day During Year
1979	100	50
1980	150	100
1981	200	150
1982	300	200
1983	350	250
1984	450	300
1985	500	400
1986	600	500
1987	700	600
1988	800	700
1989	900	800
1990	1,000	900
1991	1,100	1,000
1992	1,250	1,100
1993	1,400	1,200
1994	1,600	1,400
1995	1,800	1,600
2000	3,500	3,200

Notes: For above schedule to be achieved, it is assumed that engineering and purchasing would begin 3-1/2 to 4 years before the startup of each plant, and that construction would begin at least 3 years before plant startup. For example, if an average of 50 Mbbl/Day of shale oil is to be produced from the first plant during 1979 then this plant would have to start up early in 1979. In turn, the construction would have to begin by mid-1975, while engineering and purchasing for the plant would have to start before the end of 1974.

Table 3-5. Plausible Schedule for Buildup of Coal Liquids Production (Ref. 3-6)

Year	Nominal Capacity, Mbbl/Day at Year End	Average Production, Mbbl/Day During Year	Coal Required Million ST[a]
1980	50	-	-
1981	100	50	6
1982	200	100	12
1983	300	200	24
1984	400	300	36
1985	500	400	48
1990	1,000	900	108
1995	1,800	1,600	192
2000	3,000	2,700	324

[a] In terms of short tons of bituminous coal. Corresponding tonnages of subbituminous coal or lignite would be higher because of the lower Btu contents of these lower rank coals.

about a 19 percent/year growth rate, reflecting the fact that production of coal liquids will be started later than shale, due to the remaining technology to be developed.

Exxon points out that the production levels indicated in their tables are total liquids and not automotive transportation fuels. There will be a certain fraction of the syncrude which will be outside the gasoline and distillate boiling range. This issue will have to be considered further before making projections of total alternative automotive fuel production. Subordinate issues include: (1) trends in petroleum refinery conversion; (2) expected automotive transportation fuel demand; (3) the best way to process shale and coal syncrudes, both before 1990 when they will still be a fairly small fraction of the total crude oil and after 1990 when they could become a sizable fraction.

The outlook for liquid fuel production from organic solid waste is highly speculative. Most development and pilot plant work will be confined to utilization of municipal waste, although design studies are being made of plants to convert wood processing and logging wastes to oil. A full-scale commercial plant incorporating the Bureau of Mines hydrogenation process for either animal or wood wastes could be operational in 1980 (Ref. 2-4). The Garret pyrolysis plant in Southern California is scheduled to begin operation in 1974; it is a 200-ton-per-day demonstration plant processing municipal solid waste; the product oil will be sold to the San Diego Gas and Electric Company (Ref. 2-4). The city of Baltimore is planning to install a 1, 000-ton-per-day pyrolsis plant but the product is a low-Btu gas (Ref. 2-4). The buildup rate of oil production from such sources is expected to be slow with almost insignificant amounts by 1985. Most of this fuel will probably be sold locally for central station power generation.

3.4.2 Projected Consumer Costs

Some preliminary economic data from Exxon Research and Engineering Company are given in Table 3-6. The total cost at the service station pump (ex taxes) is the sum of: (1) the syncrude cost plus refining cost, given in the second column of the table; and (2) distribution costs, which include transportation of the syncrude to the refinery, transportation of the refined product to the service station, and the service station markup. Of these cost factors, the greatest uncertainly lies in the cost of the syncrude, since all others can be reasonably estimated from conventional petroleum product costs with minor adjustments.

The economics of a specific shale oil recovery project are quite sensitive to location, not only from the viewpoint of the richness of the shale but also reflecting water availability, shale disposal facilities, general terrain, etc. The costs associated with a substantial influx of construction and operating manpower to a sparsely populated region of the country must also be considered. The first few plants will also be more expensive due to incomplete demonstration of technology and need for

Table 3-6. Preliminary Economics of Coal and Shale[a] Fuels (Refs. 1-2 and 3-2)

FUEL	COST F.O.B REFINERY,[b] $/Million Btu	DISTRIBUTION COST,[c] $/Million Btu	TOTAL COST (EX TAXES), $/Million Btu
Gasoline from Coal	2.15	1.00	3.15
Distillate from Coal	1.50	1.00	2.50
Gasoline from Shale	1.60	1.00	2.60
Distillate from Shale	1.00	1.00	2.00
Gasoline from Petroleum[d]	2.15	1.00	3.15
Distillate from Petroleum[d]	1.80	1.00	2.80

[a] 1973 dollars, 10% DCF

[b] 100 MB/day plant

[c] Includes transportation from Western U.S. to Chicago refinery, refinery to service station; includes service station mark-up

[d] Average of current prices

equipment modifications. The effluent from the retorting operations is too viscous to be piped and will either be processed at the mine to a high quality syncrude or subjected to minimum processing at the mine to reduce viscosity to the point where it is pumpable. Except for the construction of spur lines, it is expected that existing pipelines can be used to transfer the syncrude from the first few plants either to Midwest or Gulf area refineries; the West Coast should be supplied with adequate petroleum from Alaska. Pipeline transportation costs in any event, make a relatively small contribution to the retail cost (ca. 10¢/MMBtu).

With respect to coal liquefaction, it is assumed that the industry will be associated with western strip-mined coal. This reflects the large resource base in this area as well as low mining costs. Western coal has a further economic advantage because much of it has low sulfur content. The coal syncrude can be processed by extension of conventional refining technology. The refined gasoline or distillate from both shale and coal will probably be blended with petroleum-derived analogues for quite a long time.

Cost data for gasoline and distillate from petroleum as of October 1973 are compared in Table 3-6. More recent events have brought the cost of imported petroleum to a level above the cost-plus-return-on-investment level estimated for synthetic fuels derived from domestic resources. Whether this will continue is dependent on events outside the U.S., in particular, on decisions made by the petroleum exporting countries.

3.4.3 Capital Costs and Timing Implications

Capital cost estimates are available from a limited number of sources. Reference 3-8 presents some capital requirement estimates for coal and shale derived synthetic fuels. In the former case, the basis of calculations was $7,400 per barrel-day for the first 80,000 barrel-day and

$6,500 per barrel-day thereafter. These costs apply to the liquefaction plant only. The resulting synthetic liquid plant investment for maximum production (Case I of Reference 3-8) would reach $590 million in 1980 and $4.5 billion (cumulative) by 1985. In the intermediate case, the $590 million would not be reached until 1985. Associated mine investment is difficult to ascertain from the data given, since it also includes costs to support synthetic gas plants. However, it appears that mining capital for liquefaction only would be something less than half the liquid plant costs. The statement is also made that the annual investment rate for Case I would be about $3 billion in 1985 for the coal gasification and liquefaction industry, or approximately one-third of the 1970 total combined investment rate of the chemical and petroleum industries. While no detailed study was made, such a rate of investment in 1985 appears to be feasible (Ref. 3-8).

Reference 3-9 presents plant investment costs for the H-Coal process for several ranks of coal and products produced. Capital costs run from $5,500 to $6,820 per barrel-day of product produced for a plant making about 65,000 barrel-day. Reference 3-10 gives an investment cost of $6,300 per barrel-day of coal-derived liquid for a 100,000-barrel-per-day plant, with an additional investment for a mine of $152 million or $1,520 per barrel-day. This plant uses the Solvent Refined Coal Process. It can be seen that these cost figures are in the same general range as given by the National Petroleum Council.

For oil-shale recovery, capital cost data are first quoted from Ref. 3-8. Using Case I (maximum production rate) as a basis, cumulative investment would be $4 billion for a total production of 750,000-barrel-day or $5,330 dollars per barrel-day of synthetic oil. Total industry investment would actually be about $5 billion by 1985, since 4 of 12 scheduled plants would still be under construction. The maximum annual rate of investment would be $700 million per year. It can be seen that the investment cost per barrel-day is less than for coal since the shale costs include mining costs.

The Bureau of Mines in Reference 3-11 gives a total investment cost of $426 million for a 100,000 barrel-day plant of $4,260 per barrel-day produced. For in-situ recovery, costs are $123 million for a 35,000-barrel-per-day plant or $3,520 per barrel-day of capacity; the in-situ figures are very speculative, however. The difference between the National Petroleum Council figures and those from the Bureau of Mines may be due to the fact that the former is an average value for many plants, some of which are smaller than 100,000-barrel-day; also, the first plants will probably be more expensive.

Capital investment costs for liquid-fuel production from agricultural or municipal wastes have not been documented; it is expected that they would be even more uncertain than costs for coal or shale conversion.

3.4.4 Impact With Other U.S. Energy Requirements

The liquid fuels that can be obtained from coal or shale have primary utility in the transportation sector, although they possibly could be utilized for intermediate and peak load turbines in central station electric power plants. As electric generation turns more and more to nuclear power, transportation demand will be the major utilization sector for liquid fuels. Certainly through 1985, and most probably to year 2000, combustion of conventional liquid fuels will predominate in the transportation market (Ref. 1-1); this forecast assumes no significant trend to electric cars. Thus, the major impact will be in easing U.S. requirements for imported fuels, although the degree of relief afforded by synthetic liquid fuels will be small to year 2000.

Assuming the crude oil recovery plants are located at the mines, the energy required to produce these fuels will come primarily from the local sources of coal and shale except for transportation of the products. Thus, these industries should not be significant consumers of other energy sources.

3.4.5 Factors that May Inhibit Use

There are many factors that will govern the rate of growth of these fuel sources. Obviously, economics are important, both product prices and capital investment costs. However, assuming that these factors are favorable or not limiting, other considerations may be, as pointed out in Ref. 3-8. Certainly environmental effects, at least currently, are very important, specifically strip mining of coal and spent shale disposal. For coal liquefaction, there is some technological uncertainty that may delay implementation of commercial scale plants. For shale, there is also some question of the government leasing policy for shale lands. Leasing of the first four of six 5,000-acre tracts of government-owned oil shale land in Colorado, Utah and Wyoming has recently been completed. However, the present legal restriction of 5,120 acres to any one party will prevent commercial development on an economical scale over an extended period of time. There have been recommendations from industry to at least double the acreage restrictions (Ref. 3-8). In both cases, there are logistics problems concerned with availability of trained manpower, industry's capability to supply heavy mine and plant equipment, and sufficient water resources. The intent of this listing is not so much to imply that these factors will prevent eventual development of our coal and shale resources but to indicate the complexity of such development and perhaps explain why they will not be a major source of our energy supply for many years to come.

3.4.6 Critical Technology Gaps

It has already been mentioned that coal liquefaction requires further technological advancement. The problem is not one of technical feasibility but in selection of the best unit operations, defining optimum product mixes and operating conditions, demonstrating equipment life, evaluating scaleup effects, tailoring the process to the coal characteristics, and achieving credible cost estimates for large scale plants. Solution of these problems takes time and infusion of more money, both public and private, than has heretofore been allocated. There is evidence that such funding will be forthcoming soon (Ref. 3-12). In the area of oil shale utilization, the above-ground retorting and upgrading processes are satisfactory for initial commercialization. Technical problems involve environmental considerations in spent shale and water disposal, mining, and scaleup effects; however, considerable progress has been made in these areas. In-situ processing is essentially in its infancy. At present, two in-situ research projects are under way but this approach is many years from commercial realization (Ref. 3-11).

In conversion of organic wastes, only the pyrolysis process is approaching commercial application, and most of this effort is directed toward reducing solid waste volume and generating low-Btu gas. The hydrogenation process being developed by the Bureau of Mines is barely out of the laboratory stage; economic feasibility is now being addressed. The principal technical problem is the development of methods for handling the solids and introducing them to the reactor under pressure. Other problems include refinement of the process for maximum oil yield, separation of oil from the solids, and minimization of air and water pollution. The third process, bioconversion, is less advanced than the others; since its fuel product is methane, it is outside the scope of this section (Ref. 2-4).

3.4.7 Potential for National and Regional Transportation Use

Because the synthetic petroleum-like fuels will be almost identical to the fuels now utilized in the transportation sector, the potential for employment is high if their cost is competitive. They do not, in themselves, provide lower emissions or higher efficiency in current engines but they are selectively compatible with advanced powerplants based on Brayton, Rankine, or Stirling cycles. Until such time as electric cars or hydrogen-fueled vehicles might dominate the population, these fuels will find ready markets. That time will probably be after the year 2000.

SECTION 4

METHANOL AND METHANOL-GASOLINE BLENDS

4.1 CHARACTERIZATION

4.1.1 Fuel Type

Methyl alcohol, or methanol as it is commonly called, is the hydroxyl derivative of methane with the formula, CH_3OH. It is a colorless, chemically neutral flammable liquid at ambient temperature with a mild odor. Originally derived as a by-product from destructive distillation of wood (wood alcohol) in the manufacture of charcoal, it is now chiefly prepared synthetically from hydrocarbon raw materials stemming from petroleum, natural gas, or coal sources. The earliest manufacturing process was developed in Germany and France shortly before World War I, and is still in use at the present time. It involves the catalytic hydrogenation of a synthesis gas containing carbon monoxide at elevated pressure and temperature. More recent processes are generally refinements of the carbon monoxide route. An outgrowth of the early work on carbon monoxide-hydrogen reactions led to the Fisher-Tropsch process for the manufacture of synthetic hydrocarbon fuels, alcohols, and related products.

Industrially, methanol is used chiefly as a solvent and precursor in the manufacture of plastics, resins, and organochemicals; it has been used as an automotive antifreeze, as an automotive fuel in racing, and as a reciprocating aircraft engine fuel injectant. Recently, because of lower market prices, methanol has been proposed for use as a bulk fuel to be manufactured at overseas sites where abundant natural gas resources exist. It would then be transported as a low volatility liquid (compared to LNG) and used as a fuel either in its liquid form or decomposed thermally or catalytically into combustible gases.

The methanol of commerce is generally defined according to ASTM standards in terms of purity, specific gravity, etc. A typical specification is shown (Ref. 4-1).

ASTM D1152-58 (adopted 1954; revised 1958)

Methyl alcohol (methanol) (99.85% grade) shall conform to the following requirements:

Specific gravity 20/20°C	Not more than 0.7928
Color	Not more than No. 5 on the platinum-cobalt scale
Distillation range:	
below 64.0°C	None
above 65.5°C	None
Nonvolatile matter	Not more than 0.005 g/100 ml
Odor	Characteristic, nonresidual
Water	Not more than 0.15% by weight
Acidity (free acid as acetic)	Not more than 0.003% by weight (equivalent to 0.028 mg KOH per gram of sample)
Potassium permanganate test	Color of added KMnO4 must be retained at least 30 min at 15 + 0.5°C in the dark
Acetone	Not more than 0.003% by weight

The product is shipped in one-gallon metal containers, five- or 55-gallon metal drums, or tank cars. The latter normally are loaded and unloaded by pump. Methanol can be shipped in the same tank cars used for petroleum products but precautions are taken in cleaning to prevent contamination. In dry air, the flammability ranges between 6.7 to 36 percent (by vol). Therefore, each shipping container must bear the ICC red label for "flammable liquids", and each tank car or railroad car carrying methanol must be provided with ICC "Dangerous" placards. In addition, a certain caution label, accepted by the U.S. Public Health Service, and indicating the product to be flammable and poisonous, is affixed to all containers. Other cautionary labels are prescribed by some states.

4.1.2 Reserves or Raw Material Sources

Practically any organic matter, including fermentable matter, can be used to produce gases for the direct synthesis of methanol. The primary constituent of the synthesis gas is hydrogen along with carbon monoxide and frequently carbon dioxide. This is discussed in more detail in Section 4.1.3. The most economical domestic starting materials at present are hydrocarbons derived from natural gas or naphtha. Estimates of natural gas resources total 1,412 trillion cubic feet which is equivalent to about 1450×10^{15} Btu. In addition, 6.8 billion barrels (27×10^{15} Btu) of natural gas liquids are believed to be recoverable. Crude oil reserves from which naphtha is made exist as assured reserves in the amount of approximately 36 billion barrels (210×10^{15} Btu) and, when added to estimates of undiscovered and other resources, total resources of 472 billion barrels (2739×10^{15} Btu) are projected. These liquid and gas supplies represent approximately 40 trillion gallons of manufactured methanol.

However, any future production of methanol for transportation fuel would more likely come from solid fuels as starting materials for methanol synthesis. Solid substances are more difficult to handle and process, producing undesirable solid wastes (ash) for example, or causing a greater diversion of the available thermal energy to supply the required stoichiometric amounts of hydrogen/carbon oxide gases. The primary constituent of synthesis gas is hydrogen, along with carbon monoxide and frequently carbon dioxide. Chemically bound hydrogen in reduced form is preferred as a starting raw material, but at one time the cheapest source of synthesis gas in this country was "blue gas" produced by the action of steam on coke. United States forest areas represent a potential source of organic raw material for methanol manufacture since methanol is obtained as a by-product in the distructive distillation (pyrolysis) of wood or coal, producing wood char and coke.

Coal is by far the largest and most probable single energy resource available for synthetic fuel production with an estimated total U.S. coal in place of about 3.2 trillion tons (80×10^{18} Btu). This represents a potential of about 500 trillion gallons of manufactured methanol based upon the conversion factor in Table 4-1.

In certain areas of the world where coal or lignite was abundantly available at prices highly competitive with other fossil fuel resources, coal's use as a source of methanol or liquid fuel synthesis gas was dictated in the past. Between 1936 and 1939, a total of nine plants were erected in Germany to produce synthetic liquid gasoline from coke and coal . They became obsolete after World War II (Ref. 4-1). The capacity of most of these plants was less than 200 tons/day (20 million gallons/yr), which is not large by today's standards. Japan was also using coal as a raw material source by 1939. The largest and most modern plant to use coal (low grade) as a synthesis gas source for hydrocarbons and alcohols was put into operation at Sasolburg, South Africa in 1955. This plant is still operating (Ref. 4-2).

While coal represents an extensive, available solid fuel energy resource, other solid materials also offer potential for methanol production. Shales in the western United States are believed to contain liquids in amounts up to 1780 billion barrels (10×10^{18} Btu). The practicality of converting to methanol is doubtful as it is more likely these liquids would be consumed directly as hydrocarbon fuels.

Szego, et al (Ref. 4-3) have proposed the "energy plantation" concept as a competitor to coal, using wood forests to supply energy in renewable form for electrical power generation. Correspondingly, U.S. forest areas represent a potential source of organic raw material for methanol manufacture. As previously stated, methanol is obtained as a byproduct in the destructive distillation of wood (wood alcohol) during the manufacture of wood char, but this yields a small percentage of methanol. However, steam gasification of wood char is proposed as an alternate route to synthesis gas which could be converted to methanol (thereby increasing the yield percentage). The wood processing industry produces waste residues in the form of bark, slash, sawdust, and other material. Some of this is presently used to manufacture particle board and other products, but a good deal still goes to waste. While resource availability has not been precisely defined, one

Table 4-1. Methanol Production

Energy/Material Resources	Name of the Process	Comment on the Process	Synthesized Fuel	By-Product	Thermal[a] Efficiency, %	Comments on Pollution
Coal to Methanol						
2 tons of coal (8500 Btu/lb) About 1 tone of oxygen	Use any gasifier to make synthesis gas, Lurgi and others. (Oxygen requirement varies with the process)	Coal is gasified and converted to CO + H_2-rich gas. The gas can be converted to methanol in presence of catalyst at about 40-50 atm and 200° to 300°C	1 ton of methanol	Small amount of higher alcohol is produced	50	Sulfur removal problems are similar to coal gasification problems.
SNG to Methanol						
30.2 million Btu of SNG as feed and fuel 75 kWhr power 7300 SCF CO_2 144, 016 feed water 13,200 gal cooling water	Same	Natural gas is reformed to synthesis gas. The synthesis gas is compressed to 40-50 atm and converted to methanol in presence of copper-containing catalyst at 200° - 300°C	1 ton methanol	Small amount of higher alcohol is produced	63[b]	Minimum pollution problems.
Coal or Oil Shale Derived Naphtha to Methanol						
1148 lb naphtha 9.7 million Btu fuel 58 kWhr power 1600 lb feed water 12,700 gal cooling water	Same	Naphtha is converted with steam to a CO and H_2-rich gas and then converted to methanol in presence of catalyst at 200°-300°C	1 ton methanol	Small amount of higher alcohol is produced	59[b]	Sulfur removal is necessary for feedstocks containing sulfur.
Coal or Oil Shale Derived Heavy Fuel Oil to Methanol						
2020 lb heavy oil (18, 300 Btu/lb) 130 kWhr power 1680 lb feed water 19,800 gal cooling water	Same	Heavy feedstock is converted to synthesis gas by partial oxidation and then converted to methanol in presence of catalyst at 200°-300°C	1 ton methanol	Small amount of higher alcohol is produced	50[b]	Sulfur removal problems are similar to coal gasification problems.

[a] Thermal efficiency based upon higher heating value of input and output streams, including by-products.

[b] Does not include energy involved in producing liquid or gaseous hydrocarbon raw materials from coal or shale.

estimate (Ref. 4-4) indicates that sawmill and other mill processing operations annually yield over 100 million tons of wood residues (conservatively 500 x 10^{12} Btu). Integration of methanol production plants with large wood processing plants could advantageously utilize these wastes, which represent more than 3 billion gallons of methanol per year. The key economic question to be resolved is whether the insignificant cost of waste wood as raw material would sufficiently offset plant equipment investment and product distribution costs. Other fuel studies have been started which consider the use of agricultural products as chemical raw materials. By the year 2000, up to 10 percent of domestic natural gas fuel requirements could be obtained by biological chemical conversion processes (Ref. 4-5). These gases could be used to synthesize methanol.

Examples of other sources of usable gas include by-products of industrial processes. Refinery gases containing hydrogen, metallurgical process gas, and fermentation process gases are potentially available. Methanol was once prepared synthetically by the Commercial Solvents Company from butanol fermentation gases and by DuPont from impure ammonia synthesis gases containing carbon monoxide. Generally speaking, these processes result in small plant capacities which tends to prevent them from competing against very large producers in the general chemical marketplace, although they may prove adequate for captive production. In the case of off gases from a basic oxygen furnace, economic studies have shown that the largest steel installations produce only enough off gas to support a methanol capacity of 250 tons/day or 25 million gallons/year. This is small capability by present standards. Nevertheless, as the cost of available raw materials continues to increase, the use of waste gases which otherwise have effectively zero value will become increasingly attractive.

In order for methanol to continue as a viable fuel for combustion-driven powerplants over the longer term, it could become necessary to resort to raw materials that normally exist in a partially or fully oxidized state. Hydrogen can be prepared by electrolyzing water or can be captured as a by-product from certain electrolytic processes, such as brine electrolysis.

Sources for manufacture of carbon oxides, particularly carbon dioxide, include naturally occurring carbonates in the form of limestone and dolomite deposits or even seashells. Carbon dioxide is potentially recoverable from air, in which it represents a relatively minor constitute (about 320 ppm).

A partial listing of domestic starting material sources capable of conversion to synthesis gas follows:

a. Natural hydrocarbon gases and liquids
b. Natural hydrocarbon solids - lignite and coal deposits and shales
c. Natural agricultural products - wood forests
d. Agricultural waste products
e. Industrial gases and by-products - refinery gases, metallurgical process gases, fermentation gases, SNG, electrolysis hydrogen, combustion flue gases, limestone kiln gases, and others.

4.1.3 Methods of Manufacture

There are several processes in operation for the commercial manufacture of methanol, with the basic synthesis steps represented by the equations:

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad \Delta H_{298^oK} = 21,684 \text{ cal}$$

or

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad \Delta H_{298^oK} = -11,830 \text{ cal}$$

The latter reaction may be considered to occur in two steps, viz:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

The composition of the gas mixture varies with the source material and the actual process operating conditions. Blue gas resulting from the action of steam on coke is an older route mostly replaced by steam methane reforming today. Since the latter process is current, it is covered herein, but the coke process is very similar. Steam reacts with methane to form a mixture of hydrogen, carbon monoxide, and carbon dioxide. The resulting mixture is carbon deficient, and carbon dioxide is commonly added into the process to promote the reverse-shift reaction. When higher hydrocarbons are used, a higher proportion of steam is required to prevent coking. The reactant mixture passes through catalyst-packed tubes in a furnace and, after cooling and compression, goes to the methanol converter. The pressure generally lies in the range of 50 to 400 atmospheres (750 to 6,000 psi). Recent trends have been in the direction of lower pressures using improved catalysts.

The catalytic conversion to methanol is the critical step in the process. The type of catalyst used and the operating conditions significantly influence the end-product composition. Many side reactions can take place so that a spectrum of products is possible including higher alcohols, aldehydes, ketones, hydrocarbons, etc. This is basically the Fischer-Tropsch synthesis. The key to methanol catalysis involves choosing a highly selective catalyst which does not promote carbon-carbon bond linkage. The most prevalently used catalysts are the zinc-chromium oxides and zinc-copper-aluminum oxides. In operation of the facility, several precautions are usually taken. Gases must be purified to remove such contaminants as sulfur and iron carbonyl to avoid catalyst poisoning. In addition, converter temperatures are carefully controlled and the exothermic methanation reaction, which can proceed rapidly, is avoided to prevent destroying the catalyst. In general, temperatures around 300°C are reported to result in carbon monoxide conversions of 15 percent. A typical flow sheet for the production of methyl alcohol from natural gas is shown in Figure 4-1. After the conversion step is completed, the crude methanol and water are separated by

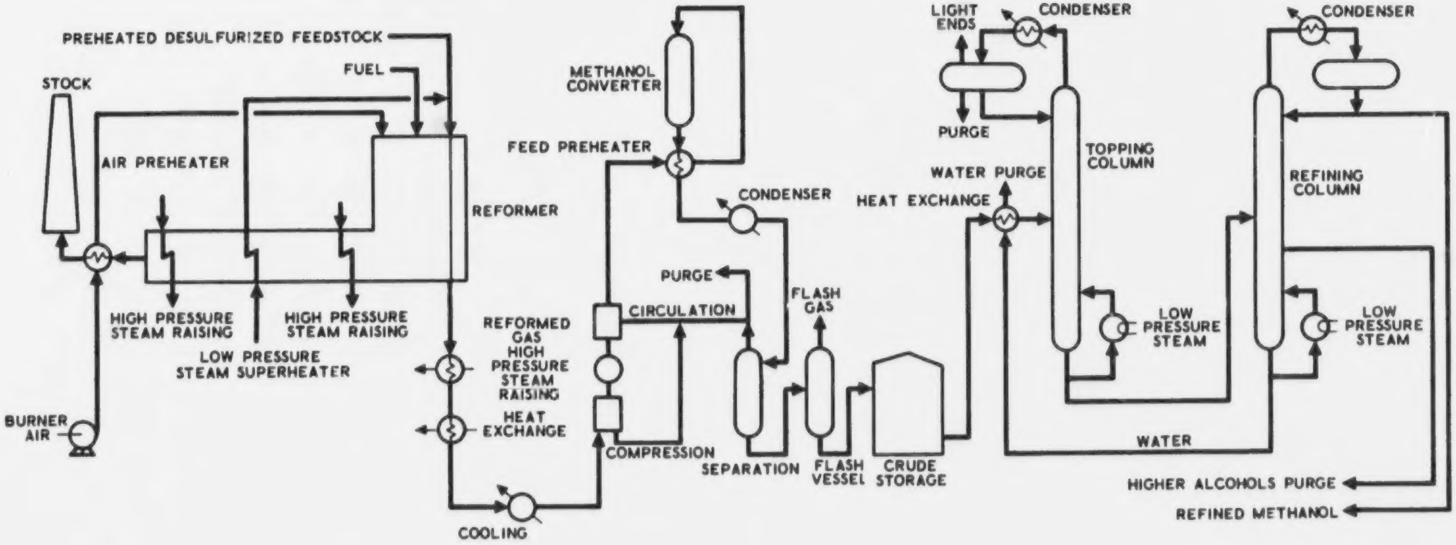

PREHEATED DESULFURIZED FEEDSTOCK
FUEL
STOCK
AIR PREHEATER
REFORMER
HIGH PRESSURE STEAM RAISING
LOW PRESSURE STEAM SUPERHEATER
HIGH PRESSURE STEAM RAISING
BURNER AIR
REFORMED GAS HIGH PRESSURE STEAM RAISING
HEAT EXCHANGE
COOLING
METHANOL CONVERTER
FEED PREHEATER
CONDENSER
PURGE
CIRCULATION
COMPRESSION
SEPARATION
FLASH GAS
FLASH VESSEL
CRUDE STORAGE
LIGHT ENDS
CONDENSER
PURGE
WATER PURGE
HEAT EXCHANGE
TOPPING COLUMN
LOW PRESSURE STEAM
CONDENSER
REFINING COLUMN
LOW PRESSURE STEAM
WATER
HIGHER ALCOHOLS PURGE
REFINED METHANOL

Figure 4-1. Methyl Alcohol Production Processes (Ref. 4-6)

condensation followed by distillation. The unreacted gases leaving the separator are partly released (purge gas) and partly combined with fresh synthesis gas to be recycled to the converter as shown.

Another similar process is the Fisher-Tropsch (F-T) process mentioned previously, which produces commercial amounts of methanol as a by-product. The major products are light gas and liquid hydrocarbons, oils, waxes, and other chemicals.

A few representative reactions involved in Fisher-Tropsch chemistry are as follows:

$$nCO + 2n\,H_2 \rightleftharpoons (-CH_2-)_n + nH_2O$$

$$2nCO + n\,H_2 \rightleftharpoons (-CH_2-)_n + n\,CO_2$$

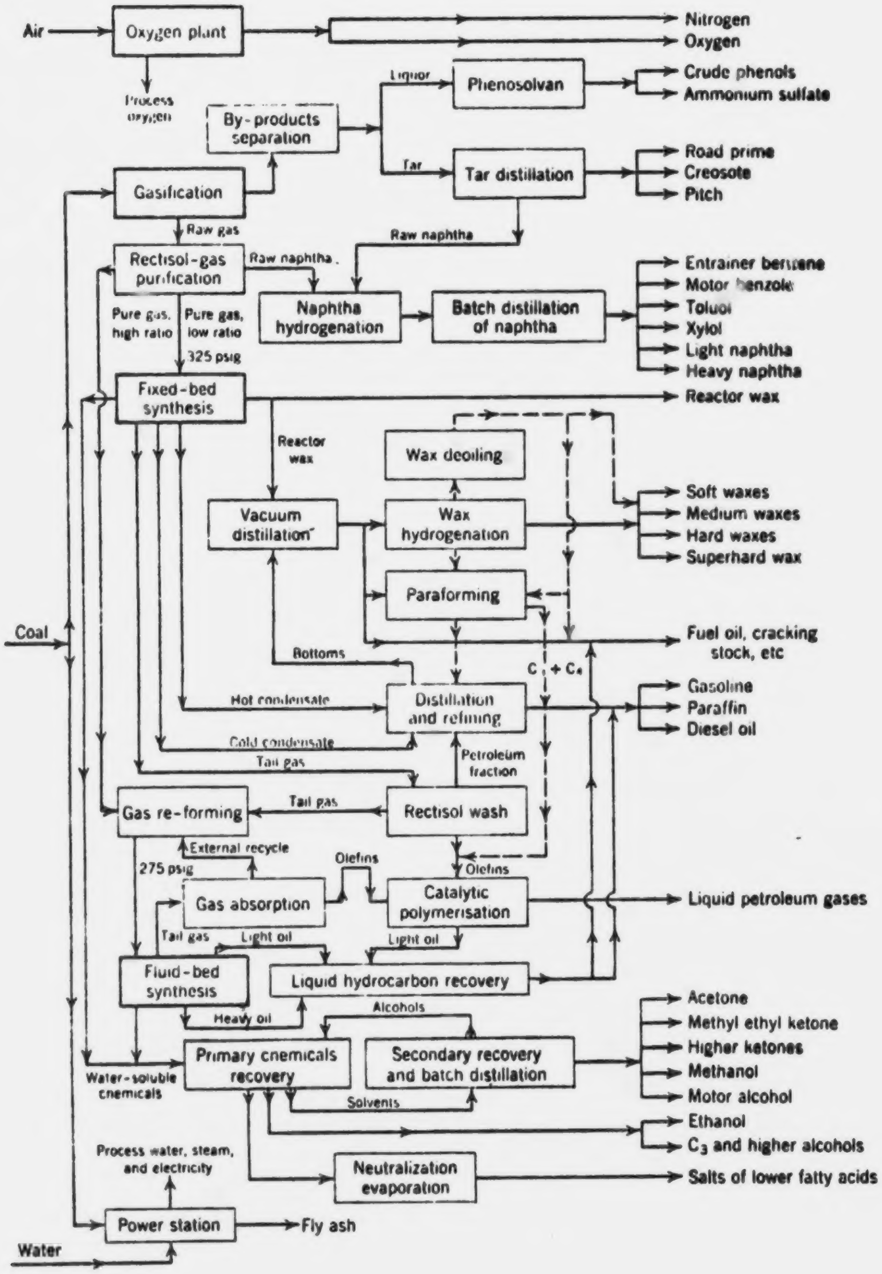
$$nCO + 2n\,H_2 \rightleftharpoons H(-CH_2-)_nOH + (n-1)H_2$$

$$CO_2 + 3H_2 \rightleftharpoons (-CH_2-) + 2\,H_2O$$

The relative extent to which these reactions proceed in the catalyst converter is somewhat controllable through catalyst selection and reactor operation. The important catalysts are Ni, Ru, Fe, and oxides such as ZnO and ThO_2. While most converter designs operate as fixed-bed reactors, fluidized-bed conversion is also practiced. The latter is used mainly with reduced iron catalyst at medium pressures. An overall picture of the Sasol/F-T synthesis process is shown in Figure 4-2.

As has already been discussed, the primary sources of feedstocks for the above synthesis routes to methanol are naturally occurring carbonaceous materials, water, and air. Several process routes are summarized in Table 4-1 for the production of methanol from coal, gaseous hydrocarbons, and liquids which can be derived from coal or shale deposits.

A two-state, liquid-phase process for low temperature hydrogenation of carbon monoxide to methanol has been demonstrated. The process



Air
Oxygen plant
Nitrogen
Oxygen
Process oxygen
Liquor
Phenosolvan
Crude phenols
Ammonium sulfate
By-products separation
Tar
Tar distillation
Road prime
Creosote
Pitch
Gasification
Raw gas
Raw naphtha
Rectisol-gas purification
Raw naphtha
Naphtha hydrogenation
Batch distillation of naphtha
Entrainer benzene
Motor benzole
Toluol
Xylol
Light naphtha
Heavy naphtha
Pure gas, high ratio
Pure gas, low ratio
325 psig
Fixed-bed synthesis
Reactor wax
Reactor wax
Wax deoiling
Vacuum distillation
Wax hydrogenation
Soft waxes
Medium waxes
Hard waxes
Superhard wax
Paraforming
Coal
Fuel oil, cracking stock, etc
Bottoms
$C_3 + C_4$
Hot condensate
Distillation and refining
Gasoline
Paraffin
Diesel oil
Cold condensate
Tail gas
Petroleum fraction
Gas re-forming
Tail gas
Rectisol wash
External recycle
275 psig
Olefins
Olefins
Gas absorption
Catalytic polymerisation
Liquid petroleum gases
Tail gas
Light oil
Light oil
Fluid-bed synthesis
Liquid hydrocarbon recovery
Heavy oil
Alcohols
Acetone
Methyl ethyl ketone
Higher ketones
Methanol
Motor alcohol
Primary chemicals recovery
Secondary recovery and batch distillation
Water-soluble chemicals
Solvents
Ethanol
C_3 and higher alcohols
Process water, steam, and electricity
Neutralization evaporation
Salts of lower fatty acids
Power station
Fly ash
Water

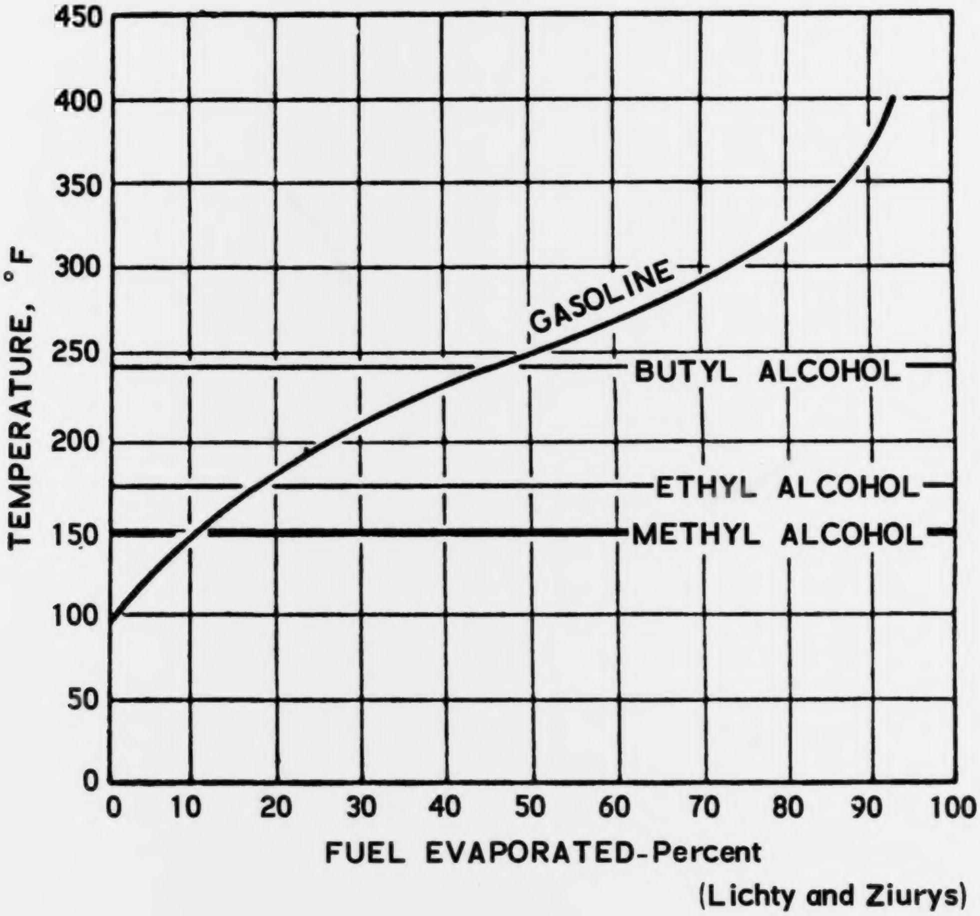
Figure 4-2. Overall Scheme of the Sasol Plant

involves the formation of methyl formate by reaction of CO on sodium methoxide solution followed by hydrogenation in the presence of copper chromite. This method has not been used commercially.

4.1.4 Physical and Chemical Properties

In terms of use as a transportation fuel, methanol properties are frequently compared to gasoline. Careful assessment of such comparisons is sometimes necessary because of the complex nature of gasolines. For example, gasolines are composed of a range of molecular species of hydrocarbons (usually C_4 - C_{10}), each of which has a different boiling point. This characteristic of gasoline results in a distillation curve which generally begins about 90°F (recovery of first distillate) and ends at about 400°F. Alcohols and other pure chemicals do not have this characteristic range of volatility. Boiling takes place at a given temperature as shown in Figure 4-3. Some of the more volatile species of gasoline begin to boil at temperatures below the boiling point of methanol. Presumably, if fuel methanol were to achieve widespread usage, it too would be marketed as a mixture of alcohols or perhaps blended with gasoline as many have suggested; however, straight methanol is also being considered. In this section, methanol is compared (see Table 4-2) with isooctane, a representative pure hydrocarbon constituent of gasolines.

Methanol has many physical and chemical properties that are similar to isooctane and, therefore, gasoline. Its heat of combustion is lower than analogous hydrocarbons because it is in a partially oxidized state. However, it also has a higher heat of vaporization and better antiknock value than isooctane. Unlike gasoline, it contains no sulfur. On the other hand, there are some disadvantages. Because its heat release is somewhat less than half that of gasoline, fuel mileage per gallon is reduced accordingly. It is also completely miscible with water, which poses the possibility of contamination and corrosion problems.



(Lichty and Ziurys)

Figure 4-3. ASTM Distillation Curves for Gasoline and Alcohol (Ref. 4-7)

Table 4-2. Properties of Isooctane and Methanol (Refs. 4-1, 4-7, 4-8, 4-9)

Item	Isooctane	Methanol
Formula	C_8H_{18}	CH_3OH
Molecular weight	114.224	32.042
Carbon to hydrogen weight ratio	5.25	3.0
Carbon, % by weight	84.0	37.5
Hydrogen, % by weight	16.0	12.5
Oxygen, % by weight	0.0	50.0
Boiling point, °F at 1 atm	210.63	148.1
Freezing point, °F at 1 atm	-161.28	-144.0
Vapor pressure, psia at 100°F	1.708	4.6
Density, 60°F, lb/gal	5.795	6.637
Coefficient of expansion 1/F at 60°F and 1 atm	0.00065	0.00065
Surface tension, dynes/cm at 68°F and 1 atm	18.77	22.61
Viscosity, centipoises at 68°F and 1 atm	0.503	0.596
Specific heat of liquid, Btu/lb-°F at 77°F and 1 atm	0.5	0.6
Heat of vaporization, Btu/lb at boiling point and 1 atm	116.69	473.0
Heat of vaporization, Btu/lb at 77°F and 1 atm	132	503.3
Heat of combustion, at 77°F		
Higher heating value, Btu/lb	20,556	9,776
Lower heating value, Btu/lb	19,065	8,593
Lower heating value, Btu/gal	110,480	57,030
Stoichiometric mixture, lb air/lb	15.13	6.463
Research octane no.	100	106

4.2 SUITABILITY FOR USE AS AN ENGINE FUEL

4.2.1 Engine/Vehicle Compatibility

Methanol has been used for many years as a gasoline additive (mainly to prevent carburetor icing) and as a power boost fluid in piston aircraft engines. Probably the two most important factors which to date have presented it from becoming a primary automotive fuel base are its low calorific value, compared to gasoline, and its higher cost. It is considered to be generally compatible for use in automotive vehicles powered by spark ignition engines except for those factors noted in succeeding paragraphs. Methanol is deemed suitable for use with continuous combustion systems (e.g., Brayton, Rankine, Stirling) and some effort has been reported regarding fuel cell applicability. It is not suitable, however, for compression ignition cycles because of its low cetane number.

From the standpoint of tankage and fuel transfer lines, corrosion inhibitors in the fuel may be necessary to prevent attach on carbon steel. Methanol is known to cause swelling of various polymers such as vinyls and acrylates but is reported to be satisfactory with certain silicones, neoprene, butyl, styrenebutadiene, and other elastomeric components.

The boiling point of pure methanol is lower than that of the bulk of the constituents of gasoline, which may result in a greater incidence of vapor lock with current automobile fuel system designs. On the other hand, the vapor pressure of methanol is substantially less than that of the very lightest ends of gasoline. The latter being responsible for the good cold start properties of gasoline, manifold preheating would probably be required for cold starts with a carburetor methanol system.

In the case of methanol-gasoline, there is an additional problem with regard to phase separation in the fuel tank. Water in the fuel distribution system or automobile fuel tank causes phase separation which in turn could lead to corrosion, rough engine operation, and starting difficulties.

Vapor lock problems may also be encountered with methanol-gasoline blends because methanol has a very high blending-vapor pressure in gasoline. The composition of the base gasoline would have to be adjusted to produce a lower vapor pressure. Then, in combination with methanol, the blend could be expected to have vapor lock characteristics no more severe than found with current gasolines.

4.2.2 Power and Fuel Economy Effects

With fixed spark-ignition engine design and operational parameters (e.g., compression ratio, displacement, fuel-air equivalence ratio,* etc.), the use of methanol instead of gasoline results in an increase in both output power and fuel consumption.

Power output is primarily determined by the heat of combustion of the fuel per unit of air consumed, plus the effect of the latent heat of vaporization of the fuel. The cooling effect caused by a higher latent heat value decreases the compression work and tends to induct a greater mass of air, thus resulting in improved volumetric efficiency. When contrasted with gasoline, methanol has both a higher combustion energy value[(1335 Btu/pound air compared to 1265 Btu/pound air for isooctane) (Ref. 4-10)]and a higher latent heat of vaporization (473 Btu/pound at boiling point and 1 atm compared to 117 Btu/pound for isooctane at the same conditions — Table 4-3). Thus, there is a noticeable increase in power output for methanol.

In the case of fuel consumption, vehicle fuel economy (miles/gallon) and engine specific fuel consumption (lb/hp-hr) are primarily a function of the heat of combustion per unit volume of fuel, with latent heat being a secondary factor only. Methanol has a much lower heating value (8, 593 Btu/pound or 57, 030 Btu/gallon) than gasoline (19, 065 Btu/pound or 110, 480 Btu/gallon) (Table 4-2). Thus when methanol is used in place of gasoline, there is an increase in fuel consumption, both in weight and volume by about a factor of two.

On the basis of miles per Btu, of course, the two fuels would be approximately equal for equivalent engine designs, sizes, and vehicle performance capability. If the effect of latent heat is considered, methanol should have a slightly better miles/Btu fuel economy than gasoline, other factors again being equal.

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* ϕ = Equivalence Ratio = fuel-air ratio/stoichiometric fuel-air ratio.

Table 4-3. Simplified Comparison of Combustion Chemistry between Methanol and Isooctane

Fuel			Intake Air		Combustion Products		Ratios			LHV, Btu/lb Air
Constituent	No. of Mols.	Weight lb.	No. of Mols	Weight lb.	No. of Mols	Weight lb.	Mols Prods / Mols Air	lb Fuel / lb Air	Gal. Fuel / Mol Air	
CH_3OH	1	32.0	7.15	206	8.65	238	1.21	0.16	0.68	1,335
C_8H_{18}	1	114.2	59.5	1,716	64	1,830	1.08	0.07	0.33	1,265

The higher antiknock quality of methanol (106 research octane number vs 100 for isooctane, see Table 4-2) will allow the use of a higher engine compression ratio for new engine designs. This can be used to further increase power output, and to increase engine thermal efficiency with concomitant beneficial effects on fuel consumption.

Predicted increases in engine power output have been calculated for methanol compared to isooctane and other fuels by detailed computer analyses (Ref. 4-8). An example of the cycle analysis results is shown in Table 4-4. At equal equivalence ratio ($\phi^* = 1$) and compression ratio (9:1), the calculated compression work for methanol (101 Btu/pound) is below that of isooctane (130 Btu/pound); the peak combustion temperature is lower (4870°R vs 5200°R), while the peak pressure is higher (1300 psia vs 1240 psia). Thus, it follows that a methanol-fueled engine can achieve power boost over a gasoline-fueled engine at the same equivalence ratio or equal power at a leaner equivalence ratio.

Table 4-4. Chart Calculations of Cycle Characteristics
C.R. = 9:1, Intake Air = 100°F, 14.7 psia (Ref. 4-8)

Fuel	Peak Temperature, R	Peak Pressure, psia	Cu Ft of Mix/ lb Air	Compression Work, Btu/lb
Isooctane, ϕ = 0.8	4820	1000	13.89	130
Isooctane, ϕ = 1.0	5200	1240	13.92	130
Isooctane, ϕ = 1.2	5170	1200	14.24	126
Isooctane, ϕ = 1.4	4910	1260	13.90	125
Methanol, ϕ = 1.0	4870	1300	13.92	101
Methanol, ϕ = 1.5	4360	1420	13.82	109
Ethanol, ϕ = 1.0	5000	1255	14.09	111
Benzene, ϕ = 1.0	5315	1265	13.98	128

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[*] ϕ = Equivalence Ratio = fuel-air ratio/stoichiometric fuel-air ratio.

As already noted, the thermal efficiency of an internal combustion engine may be improved by increasing engine compression ratio. Calculated representative effects of compression ratio on engine indicated mean effective pressure (IMEP) for methanol, isooctane, and other fuels at various equivalence ratios are shown in Figure 4-4. In general, increasing compression ratio from 8:1 to 12:1 is accompanied by 10 to 12 percent increase in power at fixed stoichiometry, or roughly equivalent fuel savings by operating with 10 to 12 percent leaner mixtures at fixed engine power.

Methanol with a research octane number of 106, compared to 100 for isooctane, can be used at a compression ratio as high as 15:1 (well above the useful compression ratio for efficient combustion of isooctane or alkyl-leaded high octane premium gasoline). However, most comparative testing in the past has been conducted with engines of modest compression ratio which may put methanol at a disadvantage from a fuel-consumption standpoint, although it does allow direct comparison with standard gasoline fuels.

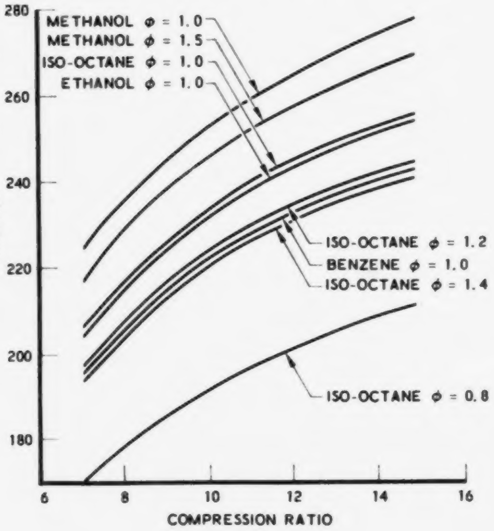

Figure 4-4. Calculated Performance Comparison (IMEP) for Isooctane, Benzene, Ethanol, and Methanol (wet charge) (Ref. 4-8)

Starkman (Ref. 4-8) obtained comparison test results with a CFR test engine operating at a 9:1 compression ratio. With this low compression ratio and injection of fuel immediately ahead of the cylinder intake, engine power output with methanol was found to exceed that for isooctane and other fuels with a corresponding penalty in specific fuel consumption as shown by Figures 4-5 and 4-6.

Ebersole and Manning (Ref. 4-9) performed an extensive fuel characterization and comparison test series with a single-cylinder CFR engine at 7.5:1 compression ratio. They showed the effects of spark timing, lean operating limits, compression ratio, and other variables on prevaporized isooctane versus methanol performance. In general, the relative specific fuel consumption figures agreed with those of Starkman. The indicated specific fuel consumption (IFSC) was found to be 2.15 times that of isooctane. The lean operating (misfire) limits were found to be about $\phi = 0.6$ for methanol versus $\phi = 0.8$ for isooctane.

Fitch and Kilgroe (Ref. 4-12) road tested a modified 6-cylinder engine powered Dodge Dart and tested a laboratory engine, both fueled with either methanol or predissociated methanol. Carburetion and manifolding modifications were made but automobile test results tended to show mostly rich operation and nonuniform distribution. Consequently, the vehicle fuel economy obtained was reduced. They reported achieving 7 to 9 miles per gallon. The spectrum of carburetor operation using different sets of fuel control jets is shown in Figure 4-7. With a main jet diameter of 0.063 inch and an air correction jet diameter of 0.060 inch, the proper equivalence mixture was reached at about 45 mph. The vehicle ran lean above this speed and rich below with this carburetor configuration. With a larger main jet (0.070 inch), operation was continuously rich.

In the laboratory engine tests, various effects were studied on a CFR engine. It was found that specific fuel consumption improves with increased compression ratio (values up to 15:1 were tried), and the engine could be operated at very lean mixture levels ($\phi = 0.65$). Specific fuel

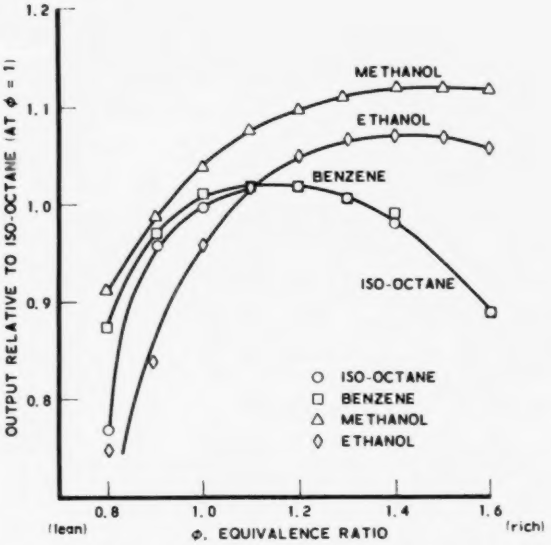

Figure 4-5. Comparative Performance Results (IMEP) from Engine Normalized about IMEP of Isooctane at $\phi = 1.0$ (Ref. 4-8)

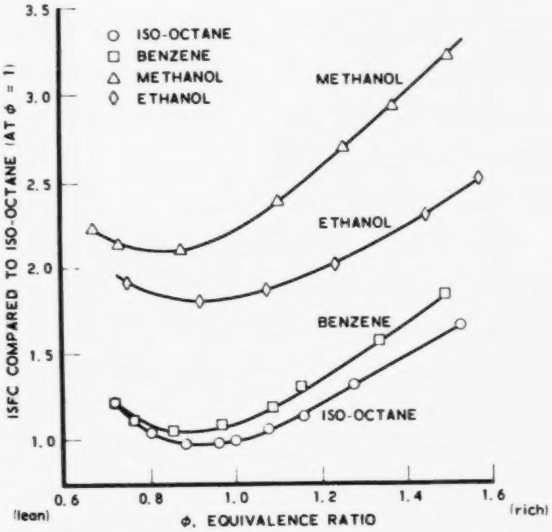

Figure 4-6. Comparative ISFC from Engine Results Normalized about ISFC of Isooctane at $\phi = 1.0$ (Ref. 4-8)

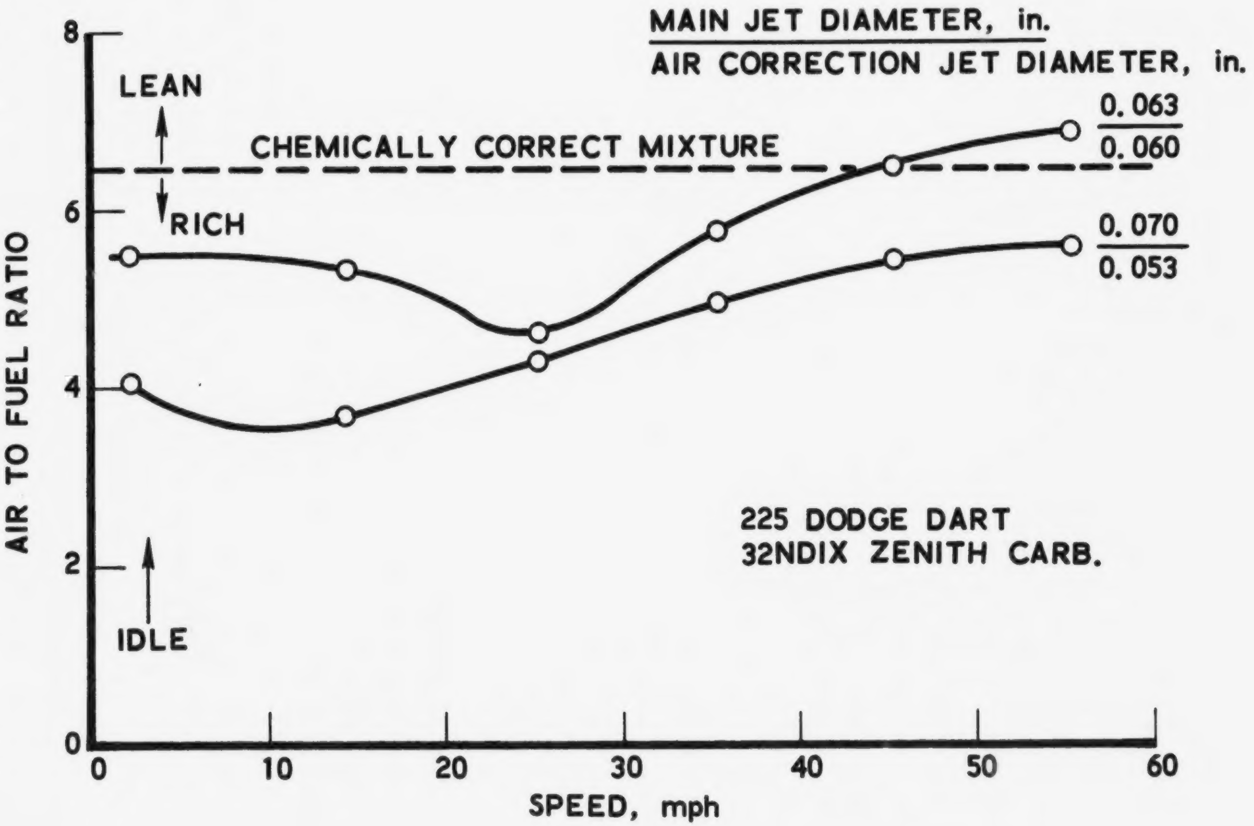

Figure 4-7. Air-to-Methanol Mixture Ratio as a Function of Speed (Ref. 4-11)

consumption was generally about 1.2 lb/hp-hr. Some slight improvement was noted with partially (thermally) dissociated methanol.

Continuation of the above effort has been reported from research at the University of Santa Clara (Ref. 4-12). A total of 191 tests were made on the CFR engine. The data were normalized for comparison between undecomposed CH_3OH, decomposed CH_3OH, and gasoline on the basis of air-fuel equivalence ratio as shown by Figure 4-8. They showed that peak power occurs at or close to the stoichiometric mixture and that thermal efficiency increases as operation varies from rich misture to lean mixtures. The fuels were prevaporized before entering the combustion chamber.

In another investigation, Stanford University modified an American Motors Gremlin to run on methanol (Ref. 4-13). Fuel economy figures for this vehicle powered by gasoline showed about 18 miles per gallon, which was reduced to 9 to 10 miles per gallon with methanol in a carbureted engine. (This is approximately as predicted by the ratio of gasoline and methanol-fuel heating values.)

4.2.3 Emission Effects

Only in the last several years has attention been drawn to investigating exhaust pollution levels attributable to methanol fuel. Studies of fuel blends containing up to 25 percent (by volume) methanol with isooctane, n-heptane, and toluene were conducted by Ford Motor Company (Ref. 4-14). Their conclusions indicated that methanol adversely affected aldehyde concentrations and unburned toluene in the exhaust under rich operation and did not improve engine exhaust quality at lean equivalence ratios ($\phi = 0.8$). The emissions appeared to be controlled primarily by the hydrocarbon constituents in the fuel. (Fuel blends are further discussed in Section 4.2.7.)

The exploratory single-cylinder engine tests conducted by Ebersole and Manning (Ref. 4-9) give perhaps the most definitive data published so far. In these tests, a 7.5:1 compression ratio was used in the CFR engine and provision was made to ensure good mixing and fuel

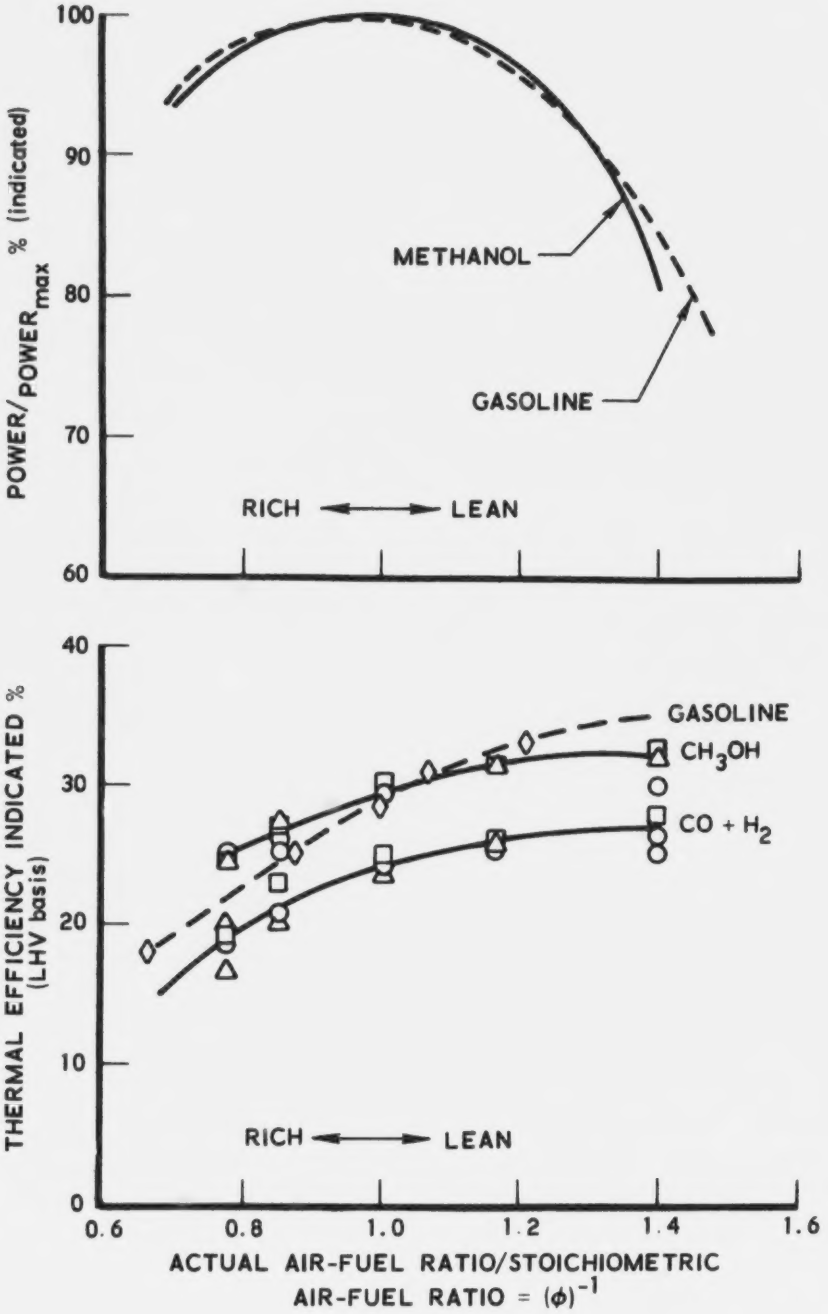

Figure 4-8. Gasoline and Methanol Performance Comparison (Ref. 4-12)

vaporization. Experimental data contour maps permit comparisons of emissions, equivalence ratio, and power obtained with prevaporized fuel-air mixtures. Several of these charts are shown for data obtained at an engine operating speed of 1,000 rpm. Figures 4-9 through 4-12 map the unburned hydrocarbons, CO, NO, and aldehydes obtained over a range of power settings and fuel-air equivalence ratios. Methanol data are superimposed over the isooctane data.

The maps represent the boundaries of conditions over which operation was found to be satisfactory (absence of misfire) up to fuel-air equivalence ratios of 1.3 (rich). The broader footprint of the methanol data graphically shows the lower lean limit of methanol operation compared to isooctane. Also shown are the nearly equal power settings.

Unburned hydrocarbons in the exhaust with methanol were 0.1 to 0.3 times that of isooctane. Undetectable levels of carbon monoxide were found at stoichiometric and leaner mixtures for both fuels. Carbon monoxide emissions with isooctane increased more rapidly than with methanol at rich operation. Trends in nitric oxide emissions between the fuels appeared comparable, tending to favor methanol at lean equivalence ratios. This was particularly evident in regions where methanol allowed operation at the same IMEP and lower equivalence ratio. For example, at an equivalence ratio for isooctane of 0.8, there were 13 to 14 g NO/ihp-hr with an IMEP of 100 psi. At the corresponding IMEP for methanol ($\phi = 0.73$) there were 8 g NO/ihp-hr, representing roughly 60 percent lower nitric oxide emissions. Aldehyde emissions increased at low equivalence ratios and were generally higher for methanol than for isooctane.

The converted Dodge Dart and the Gremlin used in the 1970 Clean Air Car Race are probably the best examples so far of modified vehicles capable of low emission operation on pure methanol. Typically, the Gremlin vehicle was able to meet the then 1975 to 1976 EPA emission standards (when equipped with a catalytic reactor) except under cold-start conditions. Emissions test data are shown in Table 4-5. The two basic engine modifications made were intended (1) to enable operation on methanol and

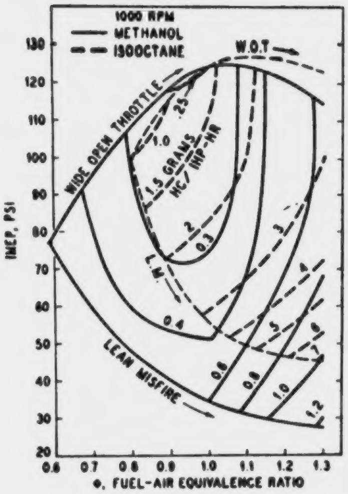

Figure 4-9. Interrelationships of Power, Equivalence Ratio, and Hydrocarbon with Isooctane and Methanol at 1,000 rpm (Ref. 4-9)

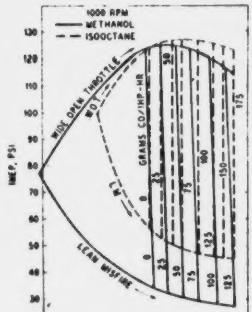

Figure 4-10. Interrelationships of Power, Equivalence Ratio, and Carbon Monoxide with Isooctane and Methanol at 1,000 rpm (Ref. 4-9)

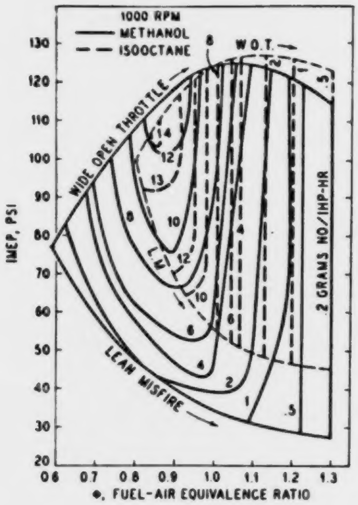

Figure 4-11. Interrelationships of Power, Equivalence Ratio, and Nitric Oxide with Isooctane and Methanol at 1,000 rpm (Ref. 4-9)

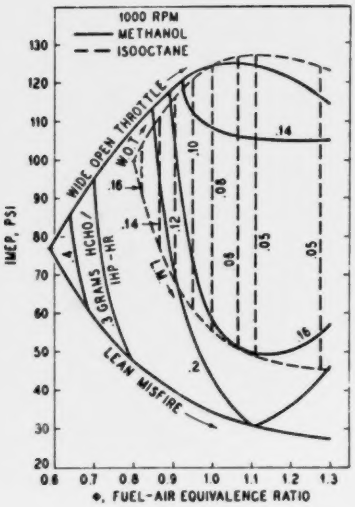

Figure 4-12. Interrelationships of Power, Equivalence Ratio, and Aldehydes with Isooctane and Methanol at 1,000 rpm (Ref. 4-9)

(2) to lower exhaust pollutants. Because methanol requires less combustion air than gasoline and has higher latent heat, larger carburetor jets and modified intake manifold heating were provided to obtain suitable vaporization and distribution of air-vapor mixtures under various loading conditions. A catalytic reactor was employed in the discharge manifold and, although an exhaust gas recirculation (EGR) system was built and tested, it was not used. The results of the tests showed that:

a. Satisfactory operation can be obtained at leaner equivalence ratios than with gasoline.

b. Unburned hydrocarbons in the exhaust consist mostly of methanol and aldehydes.

c. Low NO_x concentration results from several factors including lean, low-combustion-temperature operation, late timing, etc.

d. The catalytic muffler effectively reduces hydrocarbons, aldehydes, and CO.

e. Cold starting is difficult and causes substantial increases in emissions.

f. Further reduction in NO_x is achievable with EGR.

Table 4-5. Exhaust Emissions from Gremlin Automobile[a, b] (Ref. 4-13)

Fuel	HC g/mi	CO g/mi	NO_x g/mi
Gasoline	0.28	7.25	2.80
Methanol	0.32	3.87	0.39

[a] Hot manifold & catalytic muffler; rejetted carburetor for methanol

[b] 1972 CVS Federal Test Procedure

There appears to have been no emission work involving methanol liquid fuel-injection engines operating at a high compression ratio. The expectation from such work would be to improve lean-operating engine power and efficiency without seriously degrading pollution levels. Very little data appear in the literature concerning exhaust pollutant measurements with other engine cycles.

4.2.4 Toxicity Effects

Methanol is known to be quite toxic, producing blindness through ingestion or narcosis through inhalation. The threshold limit value for vapor is 200 ppm. This value is accepted by the American Council of Governmental and Industrial Hygienists as safe for nearly all workers under repeated exposures day after day. By observing certain precautions necessary for handling a flammable toxic material, methanol is being used safely in bulk quantities at the present time. There is a need for more information on extended lower-level exposure to methanol, such as would result from widespread use as a motor fuel.

4.2.5 Safety Effects

In terms of fire safety, methanol fires should be easier to quench than gasoline fires because of its miscibility with water. The autoignition temperature of methanol (878°F) is comparable to that for gasoline. The flash point for methanol (52°F) is lower than that of many liquid fuels but much higher than that for gasoline (-40°F).

4.2.6 Handling, Storage, and Distribution Requirements

One basic disadvantage of methanol is its miscibility with water, which requires special precautions during transport and storage to prevent contamination or adulteration. This problem is accentuated if the methanol is to be blended with gasoline, as discussed in the next section. There may also be difficulties associated with corrosion and solvent action which will emphasise proper material selection and design practices. The toxicity of methanol may impose restrictions on how it is handled at the retail level, e.g., vapor control. An educational compaign to publicize such hazards would be essential. Finally, the lower volumetric heat content of methanol as compared to gasoline would indicate the need for larger storage tanks, larger tank trucks or more frequent deliveries, increased capacity auto tanks, etc. Conversely, inasmuch as methanol is neither gaseous nor cryogenic, many features related to current gasoline storage and distribution practice could be retained with only minor modifications.

4.2.7 Methanol-Gasoline Blends

While there has been a long history of ethanol-gasoline blends usage in internal combustion engines, particularly in Europe, there as been relatively little experience with methanol-gasoline mixtures. Those favoring the use of such fuels mention the following favorable factors: (1) methanol can be made from many domestic natural resources and waste products, (2) it can thus solve the energy shortage by extending gasoline supplies, (3) the addition of methanol can reduce automotive emissions. It is difficult at this time to judge the validity of these arguments due in large part to the lack of substantiating data and to insufficient study of many important considerations such as fuel economy, exhaust emissions, engine design, vapor lock, etc. The following review briefly examines some of the issues involved, the data available, and the information required.

The fact that methanol can be synthesized from many raw materials--natural gas, petroleum, coal, oil shale, wood, and solid waste--has already been discussed in previous sections. However, the only realistic domestic source for methanol in the future appears to be coal; conversion of solid waste and forest products remain speculative, long-term sources of supplemental alcohol. Some appreciation for the magnitude of the supply problem involved can be realized from the fact that, if methanol is added at only the five percent level to gasoline, current automotive fuel consumption would require about five times present United States methanol production. Clearly, methanol is not a panacea for our present fuel shortfall. However, methanol-gasoline blends may be worth producing from coal in the future; some of the issues involved in the use of such fuels are reviewed below.

As previously discussed, methanol alone does not match the vehicle fuel economy (miles per gallon) obtainable from an equal volume or weight of gasoline because of its lower heat of combustion. However, the fuel economy comparison appears more promising when methanol is blended with gasoline at levels below about 20 volume percent. Tests quoted in Reference 4-10 showed essentially constant fuel consumption when 10 percent methanol was added to gasoline in actual road tests in automobiles of different types with normal carburetor settings. Even more favorable results are reported in Reference 4-15, where positive gains of 5 to 13 percent in fuel economy were obtained in unmodified 1966 to 1972 model cars using methanol additions of 5 to 30 percent. More specific data were given for a 1969 Toyota with an 8:1 compression ratio. All concentrations of methanol showed an improvement in fuel economy (maximum improvement of approximately 7.5 percent with 15 percent methanol). Elimination of knock and dieseling were observed even when as little as 5 percent methanol was used. The authors attribute the improvements to dissociation of methanol during the compression stroke in the engine, thereby cooling the charge and quenching premature combustion. Also, the CO and H_2 formed on dissociation increase the flame velocity, giving more complete and efficient combustion. Not mentioned was the effective leaning of the air-fuel mixture due to the fact that, although the stoichiometric fuel-air ratio for methanol is richer than that for gasoline, the same air flow rates as for gasoline were used. Additional performance improvement, using higher compression ratios and leaner operation may be feasible if unaccompanied by detrimental side effects.

Another possible advantage for methanol-gasoline blends is in exhaust emissions. Here the data are even more meager and in disagreement. The Ford Motor Company previously mentioned (Ref. 4-14) concluded that under fuel rich conditions, methanol addition increased unburned hydrocarbons in the exhaust while it had no effect under lean conditions. Previous work they cited had indicated that methanol decreases total hydrocarbon emissions. The same investigators found no change in carbon monoxide, nitric oxide,or exhaust temperature with up to 25 percent methanol, whereas

Reference 4-15 reported that CO emissions decreased from 14 to 72 percent and exhaust temperature decreased by one to nine percent with no mention of nitric oxide measurements. The fact that the various investigations utilized different types of engines, fuels, operating conditions, and analytical instrumentation undoubtedly contributed to the conflicting results.

One major problem previously mentioned in Section 4.2.1, with the use of methanol in blends (and to a lesser extent with ethanol) is the degree of miscibility in gasoline and the effect of water. The subject is summarized in Reference 4-15 and discussed at length in Reference 4-10. The solubility of methanol (and ethanol) in any hydrocarbon is function of (1) the molecular configuration and physical properties of the hydrocarbon, (2) temperature, and (3) the proportion of water present. Methanol is soluble to the least extent in the normal paraffins and to the greatest extent in the aromatics (gasoline from coal would have an advantage here). In most cases, it is more soluble in unsaturates than in naphthenes. Further, the lower the temperature, the less the miscibility, while the presence of very small quantities of water greatly reduces miscibility. Reference 4-10 states that dry methanol is miscible in all proportions with an aromatic gasoline at 60°F but only about 13 percent would dissolve in a regular gasoline and 4 percent in an all straight run gasoline. At 0°F, the methanol solubility drops to 4 percent in regular gasoline and further to about 0.5 percent with the addition of 0.03 percent water. Higher alcohols, as might be present in "methyl-fuel", are effective in increasing methanol solubility. Miscibility needs to be determined using modern gasolines, as many of the literature data are more than 20 years old.

Thus, methanol-gasoline miscibility and the effect of water on miscibility present problems both in the fuel-distribution system and in the automobile fuel tank. Several measures may be required to meet these difficulties. It appears desirable to keep the methanol and gasoline separated through the distribution system and blend of the two fuels at the service station delivery pumps. The methanol should, of course, be maintained in a "bone dry" condition to that point. To allow for temperature fluctuations and some moisture pickup in the automobile, the concentration may be limited to, perhaps, ten percent. During the winter season in colder parts of the country, it may not be feasible to market such blends at all. On the other hand, further research needed on all aspects of blend utilization in automobiles may obviate these problems through tailoring of the gasoline composition, formulation of miscibility promoters, etc.

The other potential problem mentioned in Section 4.2.1 is the possibility of encountering vapor lock with methanol-gasoline blends. Compared to its behavior when pure, methanol becomes much more volatile in hydrocarbon solutions. The result is a substantial increase in vapor pressure of a gasoline by the addition of relatively small amounts of methanol. It is predicted that an increase in vapor pressure of 3 psig (compared to an average base level of 9 psig in the summer and 12 psig in the winter), due to as little as two percent methanol, would cause significant vapor lock problems in current automobiles (Ref. 4-16). One method of correcting the problem is to remove the volatile hydrocarbons, such as butane and pentane, from the gasoline. The octane number of the resulting blend will be higher than that of the all-hydrocarbon gasoline; however, the absolute level must be experimentally determined because the octane blending value of methanol is quite variable with concentration and base gasoline type. Poor drivability could result from debutanization of the gasoline, since one function of butanes (and pentanes) is to ensure adequate fuel evaporation in the intake manifold. The higher boiling point plus high heat of vaporization of methanol could also lead to fuel maldistribution to the cylinders. These are potential problems which also need to be investigated prior to adoption of methanol-gasoline blends as automotive fuels.

As with pure methanol, methanol-gasoline blends have a higher octane rating than gasoline alone. But there are indications that the motor octane number (MON) increase is not nearly as great as that which would be expected from measured increase in the research octane number (RON). This would indicate that engine road performance increases will not be as marked as those found in the laboratory.

It is apparent from the preceding discussion that there is a need for additional investigation of all aspects of the use of methanol-gasoline blends. The advantages and potential problems need to be explored systematically to determine if there is a worthwhile net benefit in these blends and, if so, the best combination of fuel and operating conditions. The economics of not only methanol (and gasoline) production from coal but also of the impact on the distribution system needs to be explored. Until these studies are completed, it is premature to make a judgment regarding the utilization of this fuel combination.

4.2.8 Critical Research Gaps

As noted above in Sections 4.2.1 through 4.2.7, there is a definite need for additional data concerning combustion characteristics, fuel economy, and emissions for both methanol and methanol-gasoline fuel blends. The miscibility of methanol-gasoline, and the effect of water on miscibility, need to be fully evaluated, using modern gasolines, for both the fuel distribution network and the autombile fuel and engine system. The impact of methanol toxicity on fuel handling requirements needs to be explored, and the potential for achieving satisfactory methanol-gasoline vapor lock characteristics should be examined.

A program to obtain the necessary fuel economy and emissions information is being initiated by the Bureau of Mines under an interagency agreement with EPA. A range of blends, gasolines, ambient temperatures, and engines will be investigated in the test program. In addition, data will be provided on the stability of alcohol-gasoline blends and on problems connected with fuel storage and transfer.

4.3 CURRENT STATUS

4.3.1 Production Rates

Synthetic methanol production has climbed steadily in this country as shown by data in Table 4-6. Present production rates represent about one billion (10^9) gallons annually, or over 60×10^{12} Btu/year. Since

Table 4-6. Annual Synthetic Methanol Production in the United States (Source: U.S. Tariff Commission and Refs. 4-17 and 4-18)

Year	Production Millions gal/yr
1965	434
1966	494
1967	158
1968	575
1969	635
1970	744
1971	746
1972	898 (est.)

1965, the average annual increase in total output has been 11 percent and overall growth has been maintained over a much longer time period.

The production picture within the methanol industry has changed considerably over the last five years. The trend has been to eliminate marginal or noncompetitive facilities. New production capacity replacement has been achieved with larger plants. These large units have tended to improve cost economics. This has resulted mainly from new technology using the medium pressure synthesis route introduced by Power-Gas, Limited of England in 1968. Methanol producers and annual capacities of units in operation in 1972 are shown in Table 4-7.

The largest operating units are the Celanese and DuPont plants with annual capacities of 200 million gallons per year (about 2,000 tons per day). Of the 9 major manufacturers and 11 plant sites, more than 50 percent of overall capacity is concentrated in 3 plants. With the shutdown of the Union Carbide unit, the average unit capacity is 115 million gallons per year. By comparison, in 1966 there were 12 major producers with 15 plant sites and a total estimated volume of 564 million gallons per year. While this represents an average unit capacity of 38 million gallons per year, more than half of the units then operating had capacities of 25 million gallons per year

Table 4-7. U.S. Methanol Producers and Plant Capacities

Company and Plant Location	Methanol Capacity, million gal/yr
Borden Chemical	
Geismar, La.	160
Celanese	
Bishop, Tex.	90
Clear Lake, Tex.	200
Du Pont	
Beaumont, Tex.	200
Orange, Tex.	125
Georgia-Pacific	
Plaquemine, La.	100
Hercules	
Plaquemine, La.	80
Monsanto	
Texas City, Tex.	100
Rohm and Haas	
Deer Park, Tex.	22
Tenneco	
Pasadena, Tex.	80
Union Carbide	
Texas City, Tex.	42 (Shutdown was expected in 1973)
Total	1,199

or less, and only one (DuPont in Orange, Texas) exceeded 100 million gallons per year. Since that time, 10 of these plants with a combined annual output of 230 million gallons per year have ceased manufacture. It is worth noting also that by 1966, all major producers used gaseous fuels as feedstock. Earlier, coke had been a common raw material but in the period between World War II and 1966, plant shutdowns or equipment replacements eliminated coke as a raw material in the United States.

4.3.2 Users

The major uses for methanol are in formaldehyde and other chemical syntheses. Other uses include solvents, antifreezes, and fuels as shown in Table 4-8.

4.3.3 Consumer Costs

With the advent of several large production facilities which use the low pressure catalyst process, the trend of methanol manufacturing costs based on natural gas feedstock has been downward in recent years. At current prices for natural gas (ca. \$0.40/MM Btu), the sales value of methanol at the plant is on the order of \$0.10 to \$0.12 per gallon or about \$1.55 to \$1.86/MM Btu.

Exxon recently completed an economic analysis of the manufacture of methanol from coal (Ref. 4-16). A methanol-synthetic natural gas (SNG) co-product plant was examined. The SNG costs were adjusted from the 1973 National Petroleum Council report on coal availability, which considered Lurgi gasification. Depending upon the cost of coal, the scale of operation, and the relative product yield, the methanol cost (including 10 percent DCF return) was in the range of \$1.70 to \$2.35/MM Btu at the plant. For an initial 1982 scale of operation, an average methanol cost of ca. \$2.00/MM Btu was estimated. Adding on a distribution cost of \$1.90/MM Btu to account for unit train shipment from plant to terminal, truck shipment to the service stations, and the service station mark-up, the consumer price would be ca. \$3.90/MM Btu. This price was projected to fall to \$3.55 in 1990 and \$2.95 in 2000 as the scale of production increased, technology improved,

Table 4-8. Methanol End Uses, million gallons
(Refs. 4-17 and 4-20)

Uses	1960	1965	1970	1972
Formaldehyde and inhibitor	125	150	200	375
Polyformaldehyde	11	11	20	n.a.
Methacrylates	13	19	26	25
Methylamines	9	17	25	27
Dimethyl terephthalate	10	17	22	46
Methyl halides	7	11	13	28
Ethylene glycol	16	22	22	n.a.
Other chemical uses	20	25	28	n.a.
Antifreeze	10	8	5	n.a.
Solvent	20	25	28	67
Aircraft fuel injection	17	10	6	n.a.
Export	29	60	20	145
Miscellaneous	20	24	28	185
Total	297	405	450	898

pipelines replaced unit trains, etc. However, averaging cost figures from various sources, the best estimate for future costs in 1973 dollars would be about $3.40 at the pump. For comparison, IGT (Ref. 4-19) estimated methanol cost at $2.85/MM Btu based on published data but indicated the cost would probably be significantly greater. It is difficult to determine the manufacturing cost accurately without a detailed plant design study inasmuch as the scale of operation postulated is much larger than any operation to date.

4.4 PROJECTED STATUS

4.4.1 Availability

Methanol is a bulk chemical with annual production of nearly one billion gallons per year. While older, smaller, and marginally profitable production plants are being shut down, several new facilities with annual capacities on the order of 200 million gallons per year have been put onstream. In a period of about a year, four large plants with annual capacity of 600 millon gallons began to produce more than half of domestic annual production. The availability of methanol for use as a motor fuel is however, presently extremely limited.

4.4.2 Capital Costs and Timing Implications

Recent proposals have been made for jumbo size chemical plants to produce alcohol fuels from natural gas at gas well sites. For plants with production capacities of 10,000 tons per day (3 MM gal/day), invested capital estimates are on the order of $35 to $40 per daily methanol gallon capacity (Ref. 4-21). Earlier studies (Ref. 4-22) of gas feedstock plants at smaller capacity were made by A. D. Little. Their data showed invested capital for plants with 150 tons per day (45,000 gal/day) and 800 tons per day (240,000 gal/day) as $97/gallon per day and $63/gallon per day, respectively. Another study conducted in 1970 (Ref. 4-23) gave plant economics data for these capacities and 300 tons per day as well. The results of these studies are combined in Figure 4-13, corrected to 1973 dollars. These figures were compiled without distinguishing between the various types of processes, so that variations will occur in individual circumstances. Indications are that approximately three years are required for methane conversion plants to be built and begin operation. Inasmuch as natural gas is not a realistic raw material for methanol as a future transportation fuel, these data are included only as a point of reference for methanol production from coal.

Plants to convert coal to methanol will require larger capital expenditures and longer lead time, since solids handling involves costlier operation and equipment. A capital investment of $140/gallon per day for a

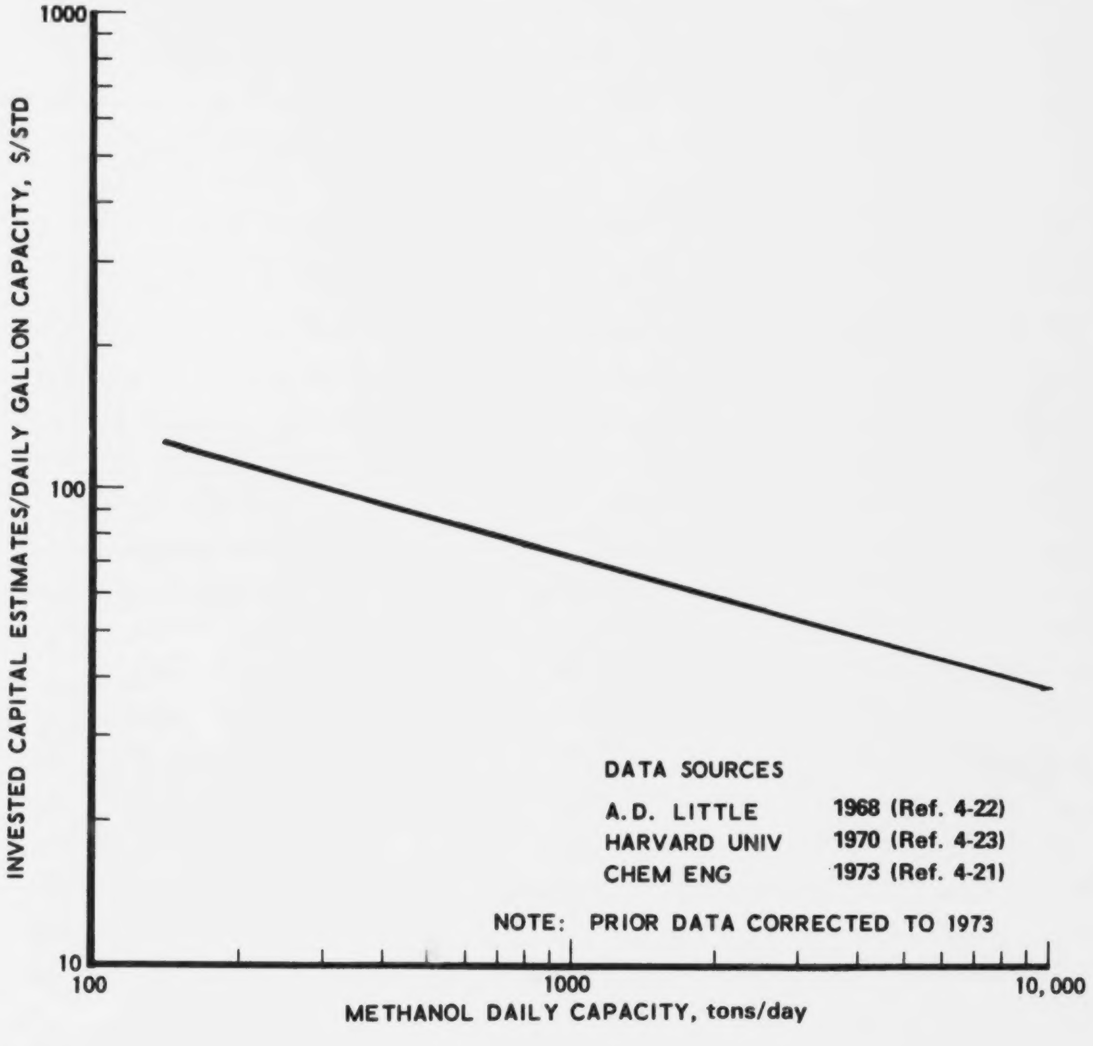

Figure 4-13. Invested Capital Cost Estimates for Methanol via Natural Gas

large methanol-from-coal plant was given by Exxon (Ref. 4-16), exclusive of distribution and marketing costs. Comparison with the data of Figure 4-13 at 10,000 tons per day capacity gives an indication of the higher investment cost when starting from coal.

4.4.3 Impact with Other U.S. Energy Requirements

Various estimates for domestic energy demand exist which show near-term average annual growth trends to be about 4 percent overall, with growth in the transportation sector trailing slightly behind. Nevertheless, an important consideration insofar as the transportation industry is concerned, is the almost entire dependence (95 percent) on the use of liquid fuels as an energy source. This situation is likely to exert a predominant influence on the trends of prime movers for future transportation conveyances (at least in the private sector). For one thing, any fuel change must be evaluated in terms of how it impacts current methods of fuel distribution between producer and consumer. Methanol, being a synthetic liquid chemical, would have a relatively minor impact for gasoline-powered vehicles, unless control methods for water exclusion from the system proves to be a formidable problem.

Attention has been turning to methanol as a liquid fuel in other energy sectors (e.g., power plants) for precisely similar considerations. Economic studies have shown that the cost of imported LNG delivered from overseas can be greater on an equivalent energy basis than methanol manufactured from the same gas for distances in excess of 12,000 miles[*] because of LNG boiloff losses (Ref. 4-24). Contributing to this situation is a rapid recent rise in costs of liquefaction equipment and cryogenic transport tankers. Methanol can be delivered in existing tankers and used as a fuel in existing equipment with only minor adjustments.

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[*] Based on cost of $0.40/MM Btu for NG at liquefaction plant.

Perhaps the most significant feature of methanol is that it can be synthesized from such a broad raw material base. The important constituent is hydrogen, presently made by reacting steam with hydrocarbons. With the greater abundance of coal, methanol as a liquid fuel supplement must be made from this source. Other starting materials, based on the indirect conversion of solar energy to plant matter or wood can possibly become practical over the long term.

4.4.4 Factors which May Inhibit Use

As has already been stated, poor fuel economy (miles per gallon) compared to gasoline and toxicity of methanol are foreseen as major factors limiting its use. In this case of methanol-gasoline blends, if satisfactory solutions to potential phase-separation problems (in storage, distribution system, and the automobile fuel tank) and vapor lock problems are not forthcoming, they would also become major use-limiting factors.

4.4.5 Critical Technology Gaps

Several gaps in technology exist pursuant to the use of methanol as an automotive fuel, although they are not seen as critical issues. One of these is the integration of large-scale coal processing plants (with improved gasification technology) and methanol synthesis plants. Perhaps a more important problem is the need for a more efficient methanol synthesis catalyst.

An area which deserves further attention involves the fact that methanol can operate at lower equivalence ratios (i.e., leaner in spark ignition engines than in gasoline-powered engines. Development programs should strive to take advantage of the high octane rating of methanol to achieve better fuel economy (miles per gallon). In fact, the whole area of methanol and methanol-gasoline performance as engine fuels needs investigation. The recent Bureau of Mines program is a good start in this direction.

4.4.6 Potential for National and Regional Transportation Use

As previously noted, the transportation industry in the United States today depends almost entirely on the use of liquid petroleum resources as an energy source. About 95 percent of the energy used in various conveyances operate on products of petroleum distillation in the form of liquids. The utilization of future fuel supplies will be dictated mainly by competition within the various consumer industries, although government policy decisions may influence how supplies are allocated. Nevertheless, it is highly unlikely that a significant proportion of transportation energy fuel demands over the near term will shift from using liquid fuels. Except for control of water absorption, increase in storage container capacity, and care in the use of solvent-resistant materials, pure methanol may be distributed in essentially the same way as gasoline. Methanol-gasoline blends may present some additional (but not insurmountable) problems if separate distribution lines and storage facilities are used for gasoline and the blending is accomplished at the terminal station. But in general methanol and methanol-gasoline blends may be considered for regional as well as national use.

SECTION 5

METHANE (NATURAL GAS AND SYNTHETIC NATURAL GAS)

5.1 CHARACTERIZATION

5.1.1 Fuel Type and Properties

Natural gas consists mostly of methane (CH_4) with relatively small amounts of other hydrocarbons (ethane, propane, butane). Nitrogen and carbon dioxide may also be present in smaller amounts. Because of supply constraints of natural gas, efforts are under way to develop the technology for deriving synthetic natural gas (SNG)* from either coal or liquid hydrocarbons. A necessary constraint is that SNG be interchangeable with natural gas as used by the power utilities industry and the transportation industry. The principal measure of equivalency is a heating value greater than 1,000 Btu/SCF.

A number of indices have been proposed to evaluate this interchangeability. They are based on the gas heating value, specific gravity, combustion air requirement, burning velocity, etc. As an example, the Wobbe Number (Ref. 5-1) is defined as the heating value of the gas divided by the square root of its specific gravity (a measure of the rate at which the thermal energy is delivered to a combustor burner tip). The coal gasification processes to be described have, in general, sufficient flexibility in the final SNG composition to ensure that such interchangeability can be preserved.

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*Also referred to as substitute natural gas.

Typical composition of natural gas and SNG as piped to consumers is shown below:

Composition of Natural Gas and Synthetic Natural Gas, % mole

	Fuel	
Ingredient	Natural Gas	Synthetic Natural Gas
Methane	89.0 - 99	88.0 - 97
Ethane	8.5 - 1.5	0.4 - 0.1
Propane	1.5 - 0.2	
CO_2/CO	0 - 0.7	1.1 - 1.3
C_4 and heavy hydrocarbons	1.2 - 0.5	
Hydrogen	0 - 0.2	10.0 - 0.8
Nitrogen	0 - 0.5	0.8 - 1.1

Table 5-1 shows some of the key characteristics of natural gas (NG), compressed natural gas (CNG), and liquefied natural gas (LNG).

The properties of natural gas (methane) are listed in Table 5-2 from Reference 4-19. For ease in transportation and storage the gas is often maintained in liquid form as LNG; therefore, both gaseous and liquid properties are quoted.

Natural gas has a density 0.6 that of air; therefore, in case of leakage in open air, it diffuses rapidly. Its ignition temperature of 1,170°F is higher than that of gasoline (approximately 700°F), but its higher vapor pressure at ambient conditions and its ability to form explosive mixtures with air require, as with any other highly flammable product, careful handling in storage and transport. Natural gas is not considered a toxic agent. Its physiological action is that of a simple asphyxiant displacing oxygen in air.

In the application of natural gas to the transportation industry, both CNG at pressures up to 3,000 psi and LNG were being used. Liquefied

Table 5-1. Key Characteristics of Natural Gas

	Gas	Liquid
Density (lb/cf)		
15 psia, 60°F	0.0449	--
3000 psia, 60°F	8.50	--
15 psia, -260°F	--	27.82
Heat of Combustion (net)		
Btu/scf	966 - 1000	--
Btu/lb	--	21,520.00
Btu/gal	--	80,000.00
Boiling Point		
15 psia, °F	--	-258.20

Gasoline Equivalence:

1 gallon of gasoline - 6.08 lb, net heat value - 117, 350 Btu

1 gallon of LNG - 3.75 lb, equivalent in Btu to 0.68 gallons of gasoline

1 cu ft CNG (3000 psi, 60°F) - 8.5 lb, equivalent in Btu to 1.56 gallons of gasoline

Table 5-2. Methane Characteristics (Ref. 4-19)

Chemical Formula	CH_4
Molecular Weight	16.041
Melting Point	-296.5°
Boiling Point	-258.5
Density	
Vapor (1 atm, 60°F); lb/ft^3	0.04243
Compressed at 2000 psi, lb/ft^3	7.08
Specific Gravity (Liquid)	0.5543
Heating Value (Vapor)	
Volumetric Gross, Btu/ft^3	1013.
Volumetric Net, Btu/ft^3	913.1
Weight Gross, Btu/lb	23,879
Weight Net, Btu/lb	21,520
Heating Value (Compressed at 2000 psi)	
Volumetric Gross, Btu/ft^3	169,065
Volumetric Net, Btu/ft^3	152,362
Weight Gross, Btu/lb	23,879
Weight Net, Btu/lb	21,520
Air for Combustion - Vapor	
Air Volumetric, ft^3/ft^3	9.528
O_2 Weight, lbs/lb	3.990
N_2 Weight, lbs/lb	13.275
Air Weight, lbs/lb	17.265
Air for Combustion - Liquid	
Air Volumetric, ft^3/ft^3	1589.9
O_2 Weight, lbs/lb	3.990
N_2 Weight, lbs/lb	13.275
Air Weight, lbs/lb	17.265

Table 5-2 (continued)

Products of Combustion - Vapor	
CO_2 Volumetric, ft^3/ft^3	1.0
H_2O Volumetric, ft^3/ft^3	2.0
N_2 Volumetric, ft^3/ft^3	7.528
CO_2 Weight, lbs/lb	2.744
H_2O Weight, lbs/lb	2.246
N_2 Weight, lbs/lb	13.275
Flammable Limits, %	5.00 to 15.00
Flame Velocity, ft/sec	1.5
Ignition Temperature, °F	1170
Theoretical Combustion Temp., °F	3484
Heat of Vaporization at Boiling Point, Btu/lb	219.22
Octane Number	115
Toxicity - Max. Allowable Concentration for Prolonged Exposure, ppm	90,000
Normal Transportation - Pipeline under pressure or as a cryogenic liquid in bulk	--

natural gas is attractive because of its greatly increased density compared to gas at atmospheric pressure (620:1) and about 3:1 higher than the density of CNG at 3,000 psi. However, the low boiling point (-260°F) requires application of cryogenic tank insulation techniques, which add substantially to automobile tank weight and cost relative to a conventional gasoline system.

The expanded use of LNG resulted in development of portable cryogenic tankage for overland and sea transportation as well as for stationary, large-volume, long-period storage facilities near metropolitan areas to meet peak demands for natural gas.

A summary of natural gas (methane) characteristics of specific interest to the transportation industry and a comparison with gasoline characteristics is shown in Table 5-3 (Ref. 2-7).

5.1.2 Reserves of Domestic Raw Material Sources

Data for domestic reserves and demand of natural gas as well as coal, which is the future raw material source for SNG, were taken from References 2-1 and 5-2. However, since these references are dealing with projections up to the year 1985[*], additional data were obtained from References 1-1 and 2-3.

The NG domestic reserves are shown in Table 5-4. The definition of ultimate gas discoverable was made by combining the volumes of past production with the estimates of the Potential Gas Committee (PGC) (Ref. 5-2). As estimated by the PGC, 62 percent of the remaining discoverable gas ($1,178 \times 10^{12}$ ft^3) is situated in the operationally difficult or frontier areas (14 percent below 15,000 feet, 20 percent offshore, and 28 percent in Alaska). The uncertainties associated with yet-undiscovered gas resources are apparent when comparing, for example, the Alaskan gas resources estimated at 272.3×10^{12} ft^3 in Reference 5-2 with those estimated at 327×10^{12} ft^3 in Reference 2-3, although both are in agreement in the total $1,178 \times 10^{12}$ ft^3 remaining. In addition, there is a possibility of utilization of nuclear devices

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[*] A brief forecast to the year 2000 is included in Reference 5-2.

Table 5-3. Relative Properties of Natural Gas (Methane) versus Gasoline for Constant Energy Value (Ref. 2-7)

		Relative lb /Btu	Relative Fuel Weight	Relative Fuel Volume	Fire Hazard Rating	Toxicity	Combustion Rating	Distribution Logistics	Tankage Cost
Gasoline		1.0	1.0	1.0	Fair	Slight to moderate	Good	Excellent	Low
Methane	Liquid	0.9	0.9	1.6	Fair	None to slight	Excellent	Fair	Fairly high
	Compr 3,000 psi	0.9	0.9	4.8	Fair		Excellent	Fair	Fairly high

Table 5-4. Natural Gas Reserves - Domestic

Units - 10^{12} ft^3 (trillion cubic feet)(Refs.2-3, 5-2)

	Ultimate Discoverable Gas	Gas Discovered to 1/1/71	Remaining	Discoverable % of Ultimate
Nonassociated				
Onshore - lower 48 states	963.1	413.1	550.0	57.1
Offshore - lower 48 states	260.1	45.9	214.2	82.4
Alaska	277.4	5.1	272.3	98.2
Subtotal	1500.6	464.1	1036.5	69.1
Associated - dissolved:				
Subtotal	356.7	215.2	141.5	39.7
Grand Total	1857.3	679.3	1178.0	63.4
Estimated addition by nuclear stimulation			317.0[a]	
TOTAL			1495.0	

[a] From Reference 2-3 (Ref. 5-2 estimates 4.6×10^{12} ft^3 for Case I, 1971 to 1985 period)

for massive fracturing of substrata which might in the future release additional quantities of natural gas from low-permeability reservoirs. The estimated amount of gas released by nuclear stimulation of 317×10^{12} ft^3 was taken from Reference 2-3 and is also included in Table 5-4.

The potential rate of domestic gas supply is shown in Table 5-5. The data are based on Case I (Ref. 5-2) which was adopted in Ref. 2-1 as the baseline condition. Case I represents a maximum effort to develop additional domestic fuel supplies and assumes oil and gas drilling increasing at a rate of 5.5 percent per year until 1985. Synthetic fuels are developed and produced at the maximum rate physically possible without any restrictions due to environmental problems, economics, etc. In short, Case I represents a most optimistic picture of domestic gas supply. For comparison, data are also shown (from Reference 1-1) which represent an intermediate approach to the gas supply forecast (average growth rate of 2.2 percent).

An important factor with regard to gas reserves for the gas industry is the ratio of proven reserves to production rate. If probable reserves of 871×10^{12} ft^3 (Ref. 2-3) are considered and an average annual rate increase from 1970 is assumed to be only 3 percent, the domestic gas reserve would be exhausted in approximately 26 years. Other forecasts are not as optimistic and, for example, it was estimated (Ref. 5-3) that, at present rates of consumption, the known reserves will be depleted in 13 years. This ratio is important for construction of any new pipeline since the Federal Power Commission (FPC) generally insists that the industry must have its reserves assured for 12 years or more in advance before a pipeline can be built (Ref. 5-4).

Irrespective of the assumed projection rates, it is obvious that the potential supply of domestic NG is insufficient and, that if the projected demand is to be met, progressively larger quantities have to be imported. The figures quoted below are solely for the purpose of illustrating the widening gap between demand and supply. The absolute values may be subject to major revisions in view of the reduced worldwide availability of fossil fuel supplies. Thus, in Table 5-5, a projected rate of increase is shown

Table 5-5. Potential Natural Gas Supply Rate

Units - 10^{12} ft^3/year[a]

	1970	1975	1980	1985	2000	
Gas, domestic production	21.80	23.70	25.90	30.60	25.00	Maximum rate of development Ref. (5-2) Case I. Data for year 2000 are an extrapolation
Synthetic (coal)	0	0	0.60	2.50	5.50	
Nuclear stimulation	0	0	0.20	1.30	1.50	
Subtotal	21.80	23.50	26.70	34.40	32.00	
Percent domestic potential energy supply	36.50	35.50	29.80	26.80	16.00	
Gas - Domestic	21.15	21.962	22.27	21.84	22.16	Intermediate rate of development Ref. (1-1)
Synthetic	0	0	0.70	2.00	5.50	
Subtotal	21.15	21.962	22.97	23.84	27.66	
Imports[b]						
Pipeline	0.90	2.00	3.00	4.10	7.40	
LNG	-	0.50	0.90	1.60	3.40	
.Imports in percent of domestic gas supply	4.00	11.40	16.90	23.90	39.00	

[a] For Btu, multiply by 1030

[b] Subject to major revision in view of the reduced world availability of fossil fuel

of gas imports from four percent of the domestic supply in 1970 to 23.9 percent in 1985 and 39 percent in the year 2000. For the optimistic supply Case I of Reference 5-2, the projected gas imported in 1985 is estimated at 17.1 percent of the domestic supply. A still worse situation exists with respect to the petroleum supply, which is not discussed in detail in this report. The shortage of gas (and petroleum products) is an incentive to search for alternative fuels such as SNG which could supplement and eventually replace NG. The production of SNG from coal is particularly attractive. A review of the domestic coal supply as a raw material source was discussed in Section 1.

The production of SNG will depend on the completion of coal gasification plants to be in operation in the post-1980 period. The predicted supply of SNG derived from coal (Table 5-5) in the year 2000 will be about 20 to 25 percent of the domestic production level of natural gas and may be expected to be of significance in replacing petroleum fuels for stationary electric generating plants.

5.1.3 Method of Manufacture

5.1.3.1 Natural Gas

The natural gas found in deposits can be either associated with petroleum, which is also called "wet natural gas" containing condensable hydrocarbons (propanes, butanes, and heavier hydrocarbons), or nonassociated dry gas free of the heavy hydrocarbons. Natural gas may be also classified as "sour natural gas" if it contains a sufficient amount of sulfur and/or carbon dioxide to be corrosive or odoriferous. "Sweet natural gas," on the other hand, does not contain these impurities. Condensable hydrocarbons removed from the wet natural gas are categorized as liquified petroleum gas (LPG).

Natural gas may also contain undesirable impurities such as CO_2, N_2, H_2O, H_2S and other compounds. A variety of processes are available for removal of these impurities (Ref. 5-5). For example, water vapor removal is based on absorption on activated solid dessicants or reactive solids. The most widely used process for removal of CO_2 and H_2S employs an aqueous solution of diethanolamine. Propane, butane, and heavy hydrocarbons are removed in a conventional oil absorption plan consisting of an absorption tower, a stripping tower, and a purification system for the by-products.

5.1.3.2 LNG

The first United States facility to liquefy and store natural gas was built in 1940. There has since been a rapid growth in the number of LNG plants and, in 1970, there were 15 plants in operation and another 9 in construction and planning stages, with a combined capacity of 750 million cubic feet per day. The rapid growth in use of LNG was brought on by its unique storage capabilities that met the needs for: (1) peaking requirements of power utilities (peak shaving), (2) providing natural gas supply for areas beyond pipelines (satellite operation), (3) enabling the transport of large quantities of gas over sea and land (baseload operation), and (4) automotive transportation applications.

Before liquefaction, the gas has to be stripped of traces of contaminants that may solidify during the liquefaction process and plug piping or four heat exchangers. Thus, water, carbon dioxide, sulfur compounds, and other natural gas constituents have to be removed. There are various dehydration processes currently in use, such as: the glycol system, amino-glycol, molecular sieves, and other dry dessicants (Ref. 5-6). Water concentration has to be reduced to approximately one part per million (0.0416 pounds of water per MM ft^3). Removal of hydrogen sulfide and the carbon dioxides is also done by various means which include: molecular sieves, amine treatment, glycol amino, Giammarco-Vetrucoke, and hot potassium carbonate. During the liquefaction cycle, the sensible and latent heat of the gas has to be removed by either cascade-cycle heat transfer through refrigerants to a heat sink, such as cooling air or water in an expander cycle cooling the gas by the work performed by it, or by modifications of these two basic cycles.

5.1.3.3 SNG (by coal gasification)

Coal gasification research in the U.S. during the last 10 to 15 years has been funded by the Office of Coal Research, the Bureau of Mines, the American Gas Association (AGA), and by private industry. Over $71 million have been spent on this research. In addition to these funds, an accelerated research program was started with joint funding of the Department of the Interior and AGA. The project will involve expenditures of approximately $300 million over the next 8 years.

There are various processes for coal gasification in the development stage, but the fundamentals of the process are common to all. The atomic ratio of hydrogen to carbon is 4:1 in methane, but only 1 :1 in coal. Consequently, to produce methane the process must include a stage to remove the excess carbon or one to add hydrogen or a combination of both. The first stage of the process, after the coal is suitably crushed and sorted (and sometimes pretreated), is the gasification stage which operates at pressures from 20 to 70 atmospheres and temperatures up to 1,500°C (Ref. 5-3). Coal is brought into contact with synthesis gas at temperatures of 600 to 800°C in the first phase of gasification. In the second phase of gasification, the devolatilized coal is brought into contact with steam at temperatures greater than 900°C to form synthesis gas of 40 to 65 percent methane. The gas mixture passes through cyclone separators to remove fine particles and dust and is then transferred to a catalytic shift converter to obtain the proper ratio of hydrogen to carbon monoxide for methane production by CO-steam reaction (Ref. 5-1). The gas then enters a purification stage in which carbon dioxide and hydrogen sulfide are removed. Then follows the catalytic methanation stage to increase the content of methane and to reduce carbon monoxide for a heating value comparable to NG (typically 1,000 Btu/cu ft). The methanation gas is then dried and, if necessary, compressed to pipeline pressures or subjected to a process of liquefication.

The basic chemistry of the process is shown in Figure 5-1 (Ref. 5-3) and the process schematic in Figure 5-2 (Ref. 5-1).

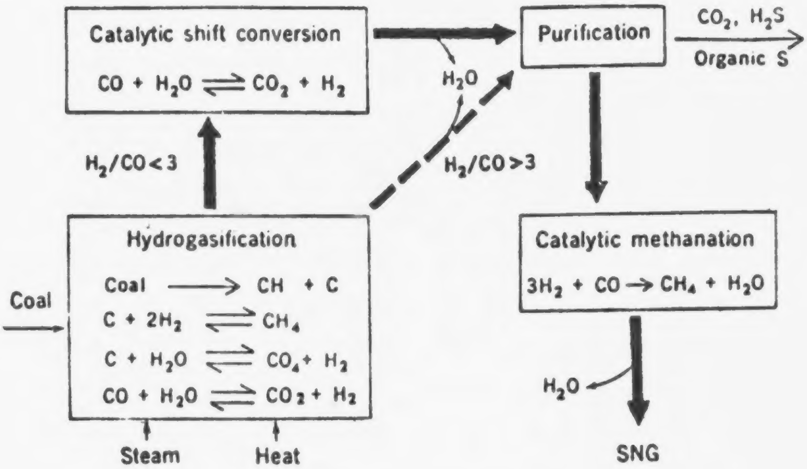
Catalytic shift conversion
CO + H2O ⇌ CO2 + H2
Purification
CO2, H2S
Organic S
H2O
H2/CO<3
H2/CO>3
Hydrogasification
Coal ⟶ CH + C
C + 2H2 ⇌ CH4
C + H2O ⇌ CO4+ H2
CO + H2O ⇌ CO2 + H2
Coal
Steam
Heat
Catalytic methanation
3H2 + CO ⟶ CH4 + H2O
H2O
SNG

Figure 5-1. Chemistry of Coal Gasification Process (Ref. 5-3)

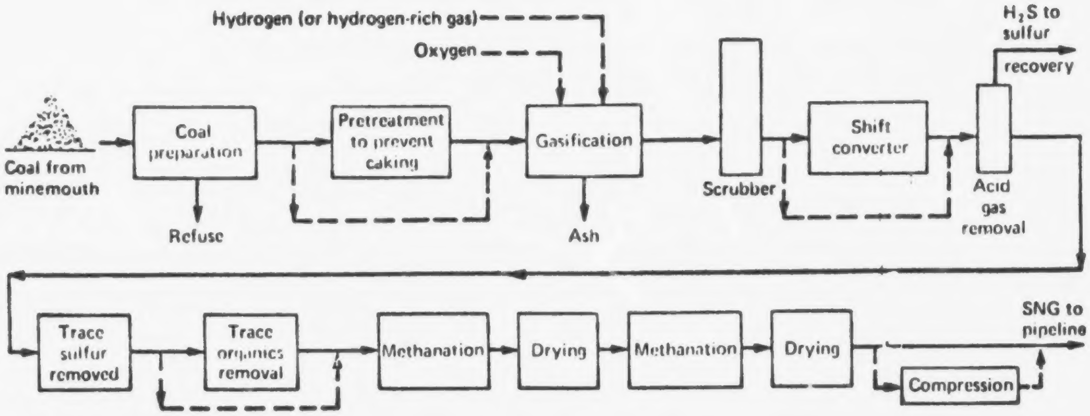
Hydrogen (or hydrogen-rich gas)
Oxygen
H2S to sulfur recovery
Coal from minemouth
Coal preparation
Refuse
Pretreatment to prevent caking
Gasification
Ash
Scrubber
Shift converter
Acid gas removal
Trace sulfur removed
Trace organics removal
Methanation
Drying
Methanation
Drying
SNG to pipeline
Compression

Figure 5-2. Process (dark lines) and Alternatives (broken lines) for Producing SNG from Coal (Ref. 5-1)

Of the several processes now under development in the U.S., the following few can be mentioned: the Hygas process developed by the AGA and the Institute of Gas Technology, the CO_2 Acceptor process developed by the Consolidated Coal Company, the Bi-Gas process developed by Bituminous Coal Research, Inc., the Synthane process developed by the U.S. Bureau of Mines; and the Lurgi process developed in Germany and adopted by several companies in the U.S. A more complete list of the various processes, including plant output levels and a description of the status and funding, is given in Table 5-6. The principal difference between the various processes is in the type of coal that can be used, the manner in which the coal is admitted to the gasifier, and the source of heat for the gasification process. In the Hygas and Synthane processes, some types of coal must be pretreated by partial volatilization to avoid conglomeration of coal particles.

Each pilot plant will also incorporate a different system for shift conversion, scrubbing, purification, and methanation, so, by the time a pilot plant is operated at 60 to 70 $MMft^3$ per day, the most economical and efficient processes will be sorted out and proven.

There are environmental problems associated with coal mining and with construction and operation of coal gasification plants. Detailed studies are being conducted; for instance, West Virginia University is conducting a study on this subject (Ref. 3-1).

The plant effluents considered necessary to control are: gases (HS, SO_2, NO_x) generated during gasification, combustion and sulfur-recovery operations; liquids consisting of process waste waters contaminated with phenols, ammonia, oil and tars; and solids consisting of fine coal dust and char.

Coal mining involves residuals in the form of aggregates and refuse as well as mine drain sludges. The plan for either disposal of the wastes as by-products or conversion into useful products must be made before a facility is constructed, and an environmental impact statement must be be approved by the appropriate agency.

Table 5-6. Summary of SNG from Coal Plants and Projects (as of April 15, 1973) (Ref. 5-7)

Name of Process	Owner(s) or Contractor and Site	Description of Process	Coal			Status and Funding
			Type	Consumption, ton/day	Plant Output 10^6 CF/day	
Lurgi Pressure Gasification (Lurgi Gesellschaft fur Warme und Chemotechnik m.b.H.)	El Paso Natural Gas Co. (Four Corners area, New Mexico)	A bed of crushed coal is introduced to the gasifier vessel through lock hoppers and travels downward as a moving bed. The process operates at pressures up to 450 psi. Steam and oxygen are introduced through a revolving steam cooled grate which also removes ash at the bottom of the gasifier. The hydrogen-rich gas passes up through the coal bed, producing some methane by hydrogenation of coal. The product gas is purified and methanated to produce 972 Btu/SCF gas.	Limited to non-caking coals	26,600	250	El Paso has announced plans for construction and operation of the Burnham Coal Gasification Complex on the Navajo Indian Reservation. Capital costs are $353.2 million for the gasification plant and 65.3 million for the associated mine. Initial gas production is scheduled for June 1976. The estimated 1977 cost of gas at the plant outlet is $1.21/MCF.
Lurgi Pressure Gasification	El Paso Natural Gas Co. (Four Corners area, New Mexico)	Same as above	Limited to non-caking coals	765	50 (Raw synthesis gas)	A single Lurgi gasifier will be installed to test improvements in the process. Goals are operation at 20% above design capacity and 30% above design pressure gasifier mechanical improvements, coal lines gasification and improved pollution control. Capital investment will be $14.1 million. First year operating cost will be $4.5 million. Completion and operation is scheduled for April 1974.
Lurgi Pressure Gasification	Texas Eastern Transmission Corp., Pacific Lighting Corp., Utah International Inc. (Four Corners area, New Mexico)	Same as above	Limited to non-caking coals	29,090	250	Texas Eastern and Pacific Lighting have made application to the FPC for authorization to construct and operate a $406.9 million coal gasification plant on the Navajo Indian Reservation near Farmington, N.M. Utah International will supply the coal and water. Plant operation is scheduled for 1976.
Lurgi Pressure Gasification	Panhandle Eastern Pipe Line Co. and Peabody Coal Co. (Illinois)	Same as above	Limited to non-caking coals	-	-	Feasibility study contract has been awarded to M. W. Kellogg and American Lurgi Corp.
Lurgi Pressure Gasification	Conoco Methanation Co. and Scottish Gas Board (Westfield, Scotland)	Methanation of purified low Btu product gas from a Lurgi pressure gasifier to demonstrate the commercial feasibility of the combination of Lurgi gasification and methanation to produce a 950+ Btu/SCF gas.	Subbituminous	-	2.6	Conoco Methanation Co. will design and construct facilities to carry out a 1 year test at a total cost of $6 million. Eleven U.S. companies are sponsoring the test which is scheduled to begin in mid 1973. The construction contractor is Woodall Duckham, Ltd.

Table 5-6 (Continued)

Name of Process	Owner(s) or Contractor and Site	Description of Process	Coal			Status and Funding
			Type	Consumption, ton/day	Plant Output 10^6 CF/day	
Lurgi Pressure Gasification	South African Coal, Oil, and Gas Corp. and Lurgi (Sasolburg, South Africa)	Methanation of the product gas from a Lurgi gasifier to produce 950+ Btu/SCF gas.	-	-	-	An experimental program to demonstrate commercial feasibility of methanation. A slip-stream from the SASOL plant will be used as feed to the methanator.
-	Texas Gas Transmission Corp. and Consolidation Coal Co.	-	-	-	-	Texas Gas Transmission Corp. has acquired one half interest in a large block of Illinois Basin coal reserves controlled by Consolidation Coal Co. The largest parcel will be held for 10 years for possible use in a coal gasification project.
-	Eastern Gas & Fuel Associates and Texas Eastern Transmission Corp.	-	-	-	-	The companies have acquired coal mining and prospecting rights to about 40,000 acres of federal and state leases in northwestern New Mexico. If the reserves are developed, Eastern Gas would conduct the mining and Texas Eastern would build and operate the gasification plant.
CO_2 Acceptor	Consolidation Coal Company (pilot plant constructed and operated by Stearns-Roger Corp.) (Rapid City, S.D.)	Coal is charged to a devolatilizer and is contacted at 300 psia with hydrogen-rich gas from a gasifier vessel. Calcined dolomite (the "Acceptor") is added to both vessels, where it reacts with carbon dioxide. "Acceptor" regeneration and ash removal is carried out in an air-blown regenerator vessel where spent char is combusted. The product gas can be purified and methanated to produce a 950+ Btu/SCF gas.	Lignite and subbituminous	40 (Pilot plant)	Up to 2 (No heating value specified)	Pilot plant undergoing start-up. A methanation stage is not incorporated, but may be added at a later date. The original pilot plant cost was about $9.3 million.
BI-GAS	Bituminous Coal Research, Inc. (Homer City, Pa.)	Coal is introduced into a reactor where it is contacted and partially gasified with hydrogen rich gas produced in the lower section of the reactor by the slagging gasification of recycle char with oxygen and steam. The pressure of operation is 1000 psia. The product gas can be purified and methanated to produce 950+ Btu/SCF gas.	All U.S. coal types	120 (Pilot plant)	2.3	Preliminary pilot plant design complete. Construction contract has been awarded to Stearns Roger, Inc. Plant cost will be about $18 million and construction will take 18 to 24 months.
Synthane	U.S. Bureau of Mines (Bruceton, Pa.)	Coal is introduced into a single reactor which incorporates three processing steps, a free fall oxygen-steam pretreatment zone, a dense fluid bed carbonizer, and a dilute fluid bed gasifier. Hydrogen-rich gas for the reaction is produced by use of oxygen in the reactor. The process operates at 500-1000 psia. The product gas can be purified and methanated to produce 950+ Btu/SCF gas.	All U.S. coal types	70 (Pilot plant)	1.4	Pilot plant design completed. Estimated cost is $10 million. Plant will be completed in December 1973. Design and consultation by Lummus Co. Construction by Rust Engineering Co.

Table 5-6 (Continued)

Name of Process	Owner(s) or Contractor and Site	Description of Process	Coal			Status and Funding
			Type	Consumption, ton/day	Plant Output 10^6 CF/day	
Kellogg Molten Salt Process	M. W. Kellogg Company	In the latest version of this process oxygen, steam and coal are injected into a high purity alumina reaction vessel where molten sodium carbonate catalyzes complete gasification of the coal. The product gas can be purified and methanated to produce 950+ Btu/SCF gas.	All U.S. coal types	-	-	OCR funded a bench scale program from 1964-1967. Total expenditures were $1.7 million. Major difficulties were experienced with materials of construction. OCR ceased sponsorship because of this problem, budgetary restrictions and assignment of higher priorities to other coal gasification processes. M. W. Kellogg has carried out additional development work since 1967, but support has not yet been obtained for construction of a large-scale pilot plant.
None	Garrett Research and Development Co. (sponsored by Colorado Interstate Gas Co.)	Coal is introduced into a simple reactor at atmospheric pressure where gas is produced by rapid devolatilization of coal. Large amounts of excess char are produced.	All U.S. coal types	-	-	Early stage of development. Being tested in small pilot plant in La Verne, California.
None	Gulf General Atomic and Stone & Webster	Coal is dissolved and the solution is hydrocracked and reacted non-catalytically with hydrogen to produce gas which is purified and methanated to 950+ Btu/SCF gas.	All U.S. coal types	-	-	Feasibility studies being made.
COGAS	COGAS Development Co. (FMC Corp., Panhandle Eastern Pipe Line Co., Tenneco Inc., Consolidated Natural Gas Service Co., Republic Steel Corp., Rocky Mountain Energy Co.)	Coal is charged to a series of fluidized-bed reactors with increasing stage temperatures to pyrolyze the coal and drive off volatile fractions in each stage. After separation of the oils and gas produced in the initial processing, the residual char is reacted with steam and air to produce a synthesis gas which is purified and methanated to a 950+ Btu/SCF gas. The operating pressure is 50 psig. The oil by product is hydrotreated to make a synthetic crude oil.	Subbituminous and bituminous	-	-	The last stage of the COGAS Process is based on results from the COED pilot plant in Princeton N.J., which was designed to produce oil, char, and a relatively small amount of gas. The COED pilot plant was funded by OCR and completed in 1970 at a cost of $4.5 million. COGAS Development Co. will invest $7 million for a pilot plant. An 18 to 24 month process evaluation is planned.
HYGAS	Institute of Gas Technology (Chicago, Illinois)	Ground, dried coal is pretreated with air, slurried with byproduct oil, and fed to a two-stage fluidized bed hydrogasifier operating at 1000-1500 psia, hydrogen-rich gas for the reaction can be furnished by processes using electric energy or oxygen, or by the stremation process. Gas from the reactor is purified and methanated to produce 950+ Btu/cu ft gas.	All U.S. coal types	75 (Pilot plant)	1.5	Pilot plant in operation. Preliminary demonstration plant design complete. Original cost of pilot plant was approximately $9.5 million.
Koppers-Tolzak	Koppers Company	Raw coal is dried, ground and charged to a gasifier by a screw conveyor with a mining head in which oxygen and steam are added to the coal fines. The reactor operates at atmospheric pressure and at 2700°F. The product gas, mostly hydrogen and carbon monoxide, can be methanated to produce 950+ Btu/SCF gas. Sixteen low Btu plants are in operation in other countries, primarily to make synthesis gas for ammonia production.	All U.S. coal types	-	-	Process is being offered in U.S. and Canada under a general license from Heinrich Koppers G.m.b.H., Essen, West Germany.

Table 5-6 (Continued)

Name of Process	Owner(s) or Contractor and Site	Description of Process	Coal			Status and Funding
			Type	Consumption, ton/day	Plant Output 10^6 CF/day	
ATGAS	Applied Technology Corp.	Coal is injected into a molten iron bath where steam and oxygen react with the carbon to produce hydrogen and carbon monoxide. The gases are then methanated to produce 950+ Btu SCF gas.	All U.S. coal types	-	-	EPA has added $222,000 to its initial contract of $820,000 for work on the high Btu gas process. A.G.A. has awarded the company $282,000 for developing a pre-pilot plant to demonstrate the process.
Union Carbide	Chemical Construction Corp. (Chemico) has been licensed by Union Carbide to use coal gasification technology developed by Union Carbide	Coal is crushed and fed to a gasifier as a dry solid or water slurry. The coal is heated in the presence of steam by direct contact with hot ash agglomerates generated by the combustion process, producing a product containing carbon monoxide, hydrogen and about 10% methane.	-	-	-	-
-	Colorado Interstate Gas Co. and Westmoreland Resources	-	-	-	-	A 10-yr option on coal reserves. Feasibility of coal gasification plant will be studied.
-	The Columbia Gas System, Inc.	-	-	-	-	Core drilling program in West Virginia to identify possibilities for coal gasification facilities 293 million tons of recoverable coal reserves have been proved on part of land on which the company has coal rights.
Self-Agglomerating Gasification Process	Battelle Columbus Laboratories (West Jefferson, Ohio)	Coal is reacted with steam in a two-stage fluidized-bed system. Air is used for combustion of part of the coal to provide heat for the gasification process. The process operates at pressures up to 100 psi to produce a synthesis gas suitable for conversion to high Btu pipeline gas by methanation.	Bituminous	-	0.8 (Synthesis gas)	Battelle has been granted a 30-month, $4.1 million contract under the joint OCR A.G.A. program.
None	Chem Systems, Inc. (Hackensack, N.J.)	A methanation process to convert coal-derived synthesis gas to high-Btu pipeline gas	-	-	-	Chem Systems has been awarded a 30 month, $1.9 million control under the joint OCR/A.G.A. program.
-	Coteau Properties (wholly owned subsidiary of North American Coal Corp.) and Michigan Wisconsin Pipe Line Co.	-	Lignite	-	-	A 20 yr option on 2.7 billion tons of North Dakota lignite to convert to synthetic gas, not before 1980's.
-	Northern Natural Gas Co. and Cities Service Gas Co. (Powder River Basin, Montana)	-	-	-	250 (Initial plant)	Northern Natural and Cities Service are considering construction of four 250 million CF/day coal gasification plants. Peabody Coal has agreed to supply about 500 million tons of coal, and the gas companies are negotiating for another. The amount of $10 million will be sent for preliminary development through 1975. Construction of the first plant could start in 1976, with operation in 1979.
-	Natural Gas Pipeline Co. of America (Dunn County, N.D.)	-	Lignite	-	-	Rights to 2 billion tons of lignite have been obtained from Star Drilling Inc. The lignite will be reserved for possible future use in a coal gasification project.

Table 5-7 provides additional information on the energy balance of the various processes. For example, in the Lurgi process the efficiency is estimated at 70 percent; of the 30 percent loss, approximately 25 percent is contained in the energy required for processing. Therefore, for three cubic feet of gas produced, one cubic foot is used for energy input.

It is expected that 35 to 40 SNG coal gasification plants, each producing approximately 250 MM ft^3/day, will be in operation by 1985 with a total output approaching 9,000 MM ft^3/day.

5.2 SUITABILITY OF NG, SNG, AND LNG FOR USE AS AN ENGINE FUEL

5.2.1 General Considerations

The large demand for petroleum products in the U.S. exceeds the domestic supply and is an incentive for implementing a search for alternative fuels derived from fossil sources.

Another incentive in the search for alternative (to liquid petroleum products) fuels is the large amount of pollutants in the form of carbon monoxide, unburned hydrocarbons, and nitric oxides, generated by heat engine prime movers using liquid petroleum products. Data for 1969 showed that 52 percent by weight of all atmospheric pollutants was contributed by transportation (Ref. 5-8). The progressively tighter Federal Emission Standards which compelled the use of various emission control devices on the conventional spark ignition engine, resulted in a 15 percent increase in fuel consumption between the vehicles meeting the 1973 and 1975 standards (Ref. 5-8). Thus, current efforts to clean up the conventional spark ignition engine, while acceptable as an interim solution, indicate the need for developing alternative fuels and alternative prime movers.

Natural gas is also in short supply, as shown earlier; but, in discussion of its long-term application to automotive vehicles, the main attention should be placed on SNG, derived from coal gasification and interchangeable with NG. All comments made on CNG or LNG operation will be, therefore, applicable to SNG.

Table 5-7. Coal to SNG (Ref. 5-18)

Energy/Material Resources	Name of the Process	Comment on the Process	Synthesized Fuel	By-Product	Thermal Efficiency, %	Comments on Pollution
355-390 billion Btu coal 4700-6500 tons O_2 19,200-28,800 tons team at 500 psi 21,600-36,000 tons/hr feed water 60 MW power⁺	Lurgi Process[2]	Lock hoppers feed crushed coal to a moving-bed gasifier. A revolving grate feeds in O_2 and steam while removing ash. Oper. pressure is up to 450 psi. Exit gas temperature is between 700° and 1100°F. This process produced 970 Btu/SCF gas. Limited to noncaking coals⁺ (incl. both electric and steam drives).	250 billion Btu	15,600 tons high-pressure steam 960-1680 tons of tar-oil-naphtha 72-144 tons phenols	70	Relatively low off-gas temperature and countercurrent design increase appearance of tars, NH_3, etc., in waste quench liquor.
17,092 tons coal (12,401 Btu/lb) as a feed and fuel (also 347,217 kW power included in it)	HYGAS Process[3] (with electrothermal gasifier)	Dried coal is slurried with light oil and fed to a 2-stage fluidized-bed hydrogasifier operating at 1000-1500 psia. An electrothermal gasifier, oxygasifier, or a steam-iron process, using char from the 2nd stage of the HYGAS unit, produces hydrogen-rich gas which is supplied for gasification. Exit gas temperature is 600°F.	253 billion Btu or 262.5 million SCF	85,104 gal oil 52,452 gal C_6H_6 81 tons NH_3	65	For the pretreatment of caking coals, sulfur existing in the pretreatment off-gas must be removed.
16,237 tons coal (12,401 Btu/lb) as a feed and fuel (also 2930 tons O_2 included in it)	HYGAS Process (with oxygen gasifier)		247 billion Btu or 256.4 million SCF	76,470 gal oil 46,339 gal C_6H_6 72.4 tons NH_3	66	
20,381 tons coal (12,401 Btu/lb) as a feed and fuel (also incl. manufacture of F_2)	HYGAS Process (with steam-iron)		253 billion Btu or 261.4 million SCF	103,152 gal oil 63,910 gal C_6H_6 99 tons NH_3	63	

Table 5-7 (continued)

Energy/Material Resources	Name of the Process	Comment on the Process	Synthesized Fuel	By-Product	Thermal Efficiency, %	Comments on Pollution
12,000 tons coal to gasifier (13,000 Btu/lb); 2400 tons coal (steam and O_2 production); 16 million gal water	Bi-Gas[4]	Coal is gasified with hydrogen. The resulting char (with O_2 and steam) produces the hydrogen-rich gas to sustain the hydrogasification process. The operating pressure is 1000 psia. Exit gas temperature is 1700°F. This process produces 950+ Btu/SCF gas. Uses all U.S. coal.	250 million SCF pipeline gas (HHV 950 Btu/SCF)	--	63	Slagging gasifiers at high temperature minimize sulfur content of the ash. High off-gas temperatures should reduce tars, amines, phenols, etc., in the quench liquor.
13,200 tons coal (13,990 Btu/lb); 226.8 tons Na_2CO_3 (makeup) 1.36 billion SCF air; 31.104 million gal cooling water (makeup); 3.785 million gal BFW	Molten Salt[5]	O_2, steam, and coal are injected into a reactor and molten Na_2CO_3 catalizes gasification. Gasifier is operated at 400 psig and 1900°F. This process produces 900+Btu/SCF gas. Uses all U.S. coal.	250 million SCF pipeline gas (914 Btu/SCF)	--	62	The sulfur is recovered during regeneration of molten salt.
14,220 tons coal (12,700 Btu/lb); 36.95 million lb h-p steam (includes production of 2770 million SCF O_2); 374.5 million gal cooling water; 25.92 million gal process water.	Synthane[6]	Coal is introduced into a single reactor which incorporates 3 processing steps; a free-fall O_2 steam pretreatment zone - a dense fluid-bed carbonizer, and a dilute fluid-bed gasifier. H_2-rich gas is produced by use of O_2 in the reactor. The process operates at 500 to 1000 psia. This process produces 900+Btu/SCF gas. Uses all U.S. coal.	250 million SCF pipeline gas (HHV 927.1 Btu/SCF)	tar 501.6 tons NH_3 88.32 tons	63	Nature of pretreatment does not produce a separate, sulfur-laden stream.
29,850 tons coal (including fuel requirements) (7068 Btu/lb); 2250 tons makeup dolomite; 1.011 billion SCF air; 2.955 million gal BFW; 159.5 million gal cooling water	CO_2 Acceptor[7]	Coal is charged to a devolatilizer and is contacted at 300 psia with H_2-rich gas from a gasifier vessel. Lime or dolomite (the Acceptor) is added to both vessels where it reacts with CO_2. This process produces 950+Btu/SCF gas. Uses lignite and subbituminous coal.	262.6 million SCF/day pipeline gas (HHV 953 Btu/SCF)	--	59	Sulfur treatment of the regenerator off-gas is required.

5.2.2 Engine/Vehicle Compatibility

Experience with the use of NG or SNG as an automotive fuel has been mainly with spark ignition engines. Since natural-gas fueling stations are practically nonexistent, the use of it is presently confined to fleet vehicles with their own depot refueling. In portable form, the gas is usually stored on-board an automotive vehicle in high pressure bottles (typically at 2400 psi) with a regulation system to reduce the pressure at the carburetor intake to a range of from 30 to 60 psi. The conversion of a gasoline engine to NG is relatively simple because, with a gaseous fuel system, the carburetor needs only to mix in the proper amount of air. The conversion consisted in many cases of a gaseous-fuel carburetor fitted on top of the existing carburetor such that, with the appropriate solenoid valves and switches, a dual-fuel operation was possible with the same ignition timing and carburetor setting (Ref. 5-9). In a dual-fuel system full advantage is not taken of high NG octane numbers (105 to 115), which permit operation at higher compression ratios and with advanced ignition timing. NG engines can also operate at leaner mixture ratios (20:1) than gasoline, and improved volumetric efficiency can be obtained with a redesigned inlet manifold. A dedicated NG system will, therefore, show an improvement in fuel economy and reduction in pollutants (HC, CO) on an energy-distance basis as compared to a dual-fuel system (Ref. 5-10). Without a leaded fuel, however, some problems may still arise with excessive valve wear. Hence, valve and valve-seat induction hardening may be required of engine manufacturers. Various fleet operators, including cities and gas utilities, have converted (starting in 1967) cars to CNG (Ref. 5-9) or LNG; and General Services Administration (GSA) has undertaken a large-scale (several thousand vehicles) conversion to natural gas, both to CNG and LNG (Ref. 5-11). Thus, over the period of the last few years, considerable experience was gathered with both CNG and LNG in automotive vehicles. While some of the details regarding fuel consumption and emissions will be discussed later it can be stated that, because of the higher volume occupied by gas (than by semivaporized gasoline in the air), there is a 10 to 15 percent drop in maximum engine power; that engine fuel consumption in miles/Btu will be approximately equal to or better than that of the modern gasoline engines equipped with emission control devices; and that exhaust emissions may be able to meet the original 1976 Federal Emission Standards except for NO_x, which may require catalytic decompostion or exhaust gas recirculation (EGR). It is also reported (in Ref. 5-12) that NG offers easy starting (even in cold weather), reliable idling, and smoother acceleration. In most vehicles, these advantages offset the disadvantage of loss in peak power.

Maintenance cost for spark ignition engines is lower for CNG and LNG than for gasoline (Ref. 5-9) because gaseous fuels burn cleanly without carbon buildup. Clean burning increases the life of the motor oil, the spark plugs, and the engine. The following data can be quoted (Ref. 5-9) representing an average of automobiles and light-duty or medium-duty trucks.

Fuel	Total Miles	Maintenance Cost, cents per mile
Gasoline	105,969	0.41
CNG	101,907	0.26

One of the problems of the conversion from gasoline to CNG or LNG is the weight and bulk of the tankage. Whether compressed to 3,000 psi or liquefied at -260°F, the fuel is less dense than gasoline, and this is well illustrated in Table 5-8. Thus, CNG tankage plus fuel equivalent to 20 gallons of gasoline will weigh approximately 350 pounds more and occupy 5.5 times more volume than a gasoline system. LNG will require an additional 100 pounds weight and occupy approximately 2.2 times the volume of gasoline including tankage provisions. The size of the tank required for NG vehicles depends on the type of operation, but fleet operators think that a daily range of 100 to 125 miles is sufficient.

Both high-pressure tanks for CNG and cyrogenic tanks for LNG are available commercially in various sizes. With LNG, certain boiloff loss

Table 5-8. Tankage Comparison
(Refs. 2-1, 5-18)

Basis: Energy Equivalent of 20 gals gasoline[a]
(2.27×10^6 Btu)

	Fuel Alone		Fuel + Container	
	lbs.	ft^3	lbs.	ft^3
Gasoline[b]	119	2.59	134	2.76
No. 2 Diesel Fuel[c]	120	2.28	134	2.50
Methane (gas) @ 3000 psi, 80°F	105.5	12.40	500	14.6
Methane (liquid) @ 1 atm	105.5	4.06	240	6.1

[a] On an equal mileage basis (i.e., 270 miles) the fuel storage requirements must be adjusted for the thermal efficiency of the vehicle. In the case of diesel power the above figures would be reduced by 1/3.

[b] This assumed to apply to all gasolines whether from petroleum, coal, or shale.

[c] This assumed to apply to all distillate fuels whether from petroleum, coal or shale.

when the vehicle is nonoperating becomes unavoidable and is of the order of 3 to 4 percent per day. This must be added to the operating cost of LNG.

The cost of conversion of medium-size gasoline vehicles to CNG or LNG was about $300 to $500 (the lower figure for CNG), but this cost and the cost of refueling equipment was amortized in California Institute of Technology operations in approximately five years because of savings in maintenance and in fuel cost (Ref. 5-9) in a dual fuel system using 20 percent gasoline and 90 percent CNG. With 100 percent CNG use, these costs would be paid off in four years because of the low cost of CNG.

The characteristics of operation with natural gas (or SNG) of a spark ignition engine (that is, cleaner combustion with low emission of pollutants, high combustion efficiency, and possibility of operation at lean air-fuel mixtures, as well as the storage problems) will apply to other engine cycles. Automotive vehicle compatibility with natural gas used as fuel for various engines is given in Table 5-9.

5.2.2.1 Wankel Engine

The Wankel engine is characterized by high fuel consumption, high hydrocarbon and carbon monoxide emission, low thermal efficiency, and low oxide of nitrogen emission compared to Otto cycle spark ignition engines. Its advantage lies in its small size and weight. Its operation with natural gas (or SNG) is expected to be similar to that of Otto cycle spark ignition engines.

5.2.2.2 Brayton Cycle Engine

Brayton cycle engines, represented by gas turbines, have inherent fuel versatility. They have been run on methane with oxide of nitrogen emissions much lower than those with gasoline or propane (Ref. 2-1).

5.2.2.3 Rankine Cycle Engine

Rankine cycle engines use an external source to heat a working fluid for conversion into work. The heat source may be solar or fossil fuel energy; consequently, natural gas with its clean combustion and lean mixture

Table 5-9. Automotive Vehicle Compatibility with Natural Gas when Compared with Gasoline Fuel (Ref. 5-18)

Engine Type / Fuel	Spark Ignition Otto Cycle	Stratified Charge	Diesel	Gas Turbine	Rankine	Stirling
Gasoline	No modification	Pilot injection. High compression ratio for satisfactory ignition.	Major modification	No modification	No modification	No modification
Natural gas (methane)	Major modification. Bulky fuel storage.	Major modification. Bulky fuel storage.	Major modification. Pilot injection of high octane number fuel.	Major modification. Bulky fuel storage.	Major modification. Bulky fuel storage.	Major modification. Bulky fuel storage.

operation may show an advantage over gasoline, but no data are available as yet to substantiate this expectation.

5.2.2.4 Stirling Cycle Engine

Stirling engines use an external heat source, and the same comments apply as to the Rankine engine.

5.2.2.5 Stratified Charge Engine

The stratified charge engine utilizes high pressure fuel injection or dual carburetors. With injection, combustion is nearly immediate after injection and this frees the engine from the need for high octane fuels; however, there is probably a minimum cetane number (maximum ignition delay) requirement. Fuels generally run in stratified charge engines range from methane to No. 2 diesel fuel. Tests have been run with methane by Curtiss-Wright without difficulty, but no emission data are available.

5.2.2.6 Diesel Engine

Diesel engines are more efficient engines because of very high compression ratios. Gaseous fuels are not injected into diesel engines in the same way as liquid fuels (Ref. 2-1). Methane (or propane), when used in diesel engines, is inducted with the air, compressed, and finally ignited by the injection of high-cetane fuel. This scheme is very similar to the spark ignition process. Compression ratios are limited to 14:1. Power is slightly lower than that of a diesel engine with the same compression ratio.

5.2.3 Fuel Economy

Although a substantial number of motor vehicles are operating now in the U.S. on CNG or LNG, the data on fuel consumption are relatively meager. One source (Ref. 5-13) quotes, for example, over 3,000 CNG and 500 LNG motor vehicles operating in the U.S. in 1972. Data on fuel consumption of GSA vehicles demonstrated almost the same fuel consumption in miles/gallon for LNG and gasoline (9.15 to 9.3 mpg). Other findings were reported in the SAE Engineering Congress in January 1972, where a paper cited 16 percent loss (on a mile/Btu basis) for CNG fueled cars (quoted in Ref. 5-13).

Reference 5-14 quotes a 50,000-mile road test under varying climatic conditions with a 1968 Dodge Dart and a 1968 Ford Fairlane, both converted to LNG. The conversion was relatively simple. A 21-gallon, double-walled, vacuum-jacketed vessel was installed for the fuel tank and operated at pressures of 40 to 60 psia so there was no need for a pump. Compression ratio was increased from 8.00 to 9.75 to take advantage of LNG high octane number (>105), and a commercially available natural gas carburetor was substituted for the gasoline carburetor with a fuel vaporizer tube fitted into the carburetor intake. The fuel consumption test results are shown below.

	Dodge	Ford
Gasoline	17.8 mpg	15.3 mpg
LNG	15.4 mpg	13.9 mpg

- Gross heating value for gasoline - 120,000 Btu/gal
- Gross heating value for LNG - 90,000 Btu/gal

"The consensus of operational experience with natural gas has been that 100 cubic feet (lower heat value 100,000 Btu) are equivalent in average driving to one gallon of gasoline," McJones and Corbell (Ref. 5-10). This result is generally consistent with fuel-consumption data for vehicles operated on a seven-mode driving cycle. Results are given in Table 5-10 showing Btu/mile with NG running from 80 to 100 percent of gasoline values, a 90-percent average.

The operation with natural gas is particularly advantageous in city driving where the absence of an accelerator pump and the very lean mixtures at idling contribute to Btu/mile figures lower than for gasoline.

Tests with single and multi-cylinder engines carried out in Reference 5-12 with gasoline and CNG have shown that the CNG engine could operate with lean mixtures up to air-fuel ratio of 25:1 (equivalence ratio* of 1.5),

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*Actual air-fuel ratio/stoichiometric air-fuel ratio = $(\phi)^{-1}$

Table 5-10. Vehicle Identification, Fuel Consumption, and Carbon Dioxide Data (Ref. 5-10)

Engine Class Cubic Inch Displ.	Yr/Cyl Displ. Trans.	Test Conditions	Odometer Mileage	Gasoline		Natural Gas		Natural Gas[a] CO_2 Reference %	Btu/Mile Nat. Gas/Gasoline
				Fuel g/mi	CO_2 g/mi	Fuel cu ft/mi	CO_2 g/mi		
(a) 0-140	1969/4	Baseline	3997	128.0	405	—	—	—	—
	134 c.i.	At conversion	3295	131.0	415	4.58	263	9.5	0.84
	Man.	After 4000 mi.	7298	127.2	403	4.86	279	10.4	0.91
(b) 140-250	1969/6	Baseline	3081	153.6	487	—	—	—	—
	199 c.i.	At conversion	3990	170.0	539	5.46	313	8.7	0.77
	Man.	After 4000 mi.	8402	180.0	571	6.08	349	9.2	0.81
(c) 200-250	1968/6	Baseline	9541	176.0	558	—	—	—	—
	250 c.i.	At conversion	10559	205.0	650	7.84	450	10.4	0.92
	Man.	After 4000 mi.	14123	195.5	620	7.92	454	11.0	.97
(d) 250-300	1968/8	Baseline	3172	—	—	—	—	—	—
	289 c.i.	At conversion	4987	—	—	—	—	—	—
	Auto.	After 9000 mi.	14060	173.0	548	7.2	413	11.3	1.00
(e) 300-375	1969/8	Baseline	3097	213.0	676	—	—	—	—
	302 c.i.	At conversion	5443	236.0	748	9.62	552	11.0	0.98
	Auto.	After 4000 mi.	9754	222.0	704	8.66	497	10.6	0.93
(f) 375 +	1967/8	Baseline	41188	267.0	846	—	—	—	—
	440 c.i.	At conversion	44933	267.0	846	9.61	552	9.8	0.86
	Auto.	After 4000 mi.	49097	267.0	846	10.26	588	10.4	0.92

[a] Natural gas CO_2 reference is calculated as 15% × $\frac{CO_2 \text{ nat. gas}}{CO_2 \text{ gasoline}}$ and is presented as verification of the 11% value adopted by the California ARB for natural gas exhaust dilution corrections.

while the lean mixture limit for gasoline was 19.5:1 (equivalence ratio of 1.35). The minimum fuel consumption of CNG engines was at air-fuel ratios between 19 and 20 and was improved with an advance in ignition timing. On the other hand, HC and NO_x emissions decrease with retarded ignition and leaner mixtures. Consequently, a compromise setting in air-fuel and ignition timing has to be made for low emissions with acceptable fuel economy.

Summarizing the data quoted, it appears that, due to higher combustion efficiency (better mixing) of natural gas and its ability to operate at leaner mixtures (up to 1.45 equivalence ratio), a CNG or LNG engine may have a lower expenditure of Btu/mile than 1968 model year engines. The addition of more extensive emission control devices on later car models may further tip the scale in favor of natural gas fueled engines which may require only a device for suppression of NO_x.

The result of this improved efficiency is a fuel-cost savings, assuming that with continued price regulation the cost of 100 cubic feet of NG in the form of CNG will be $0.157 at the pump; a gallon of LNG will be $0.245, compared with a gallon of medium-octane gasoline at $0.265.* With a medium-size automobile driven, say, 15,000 miles per year and equal consumption per gallon of gasoline = 100 cubic feet of natural gas,** at 13 miles per gallon, the assumed fuel saving alone between gasoline and CNG would be approximately $125 per year. To this should be added engine maintenance savings previously discussed in this section.

5.2.4 Emission Effects

In contrast to the consumption data, a substantial amount of information has been published on exhaust emissions for various automotive engines operating on NG (both CNG and LNG). The data vary depending on the type of vehicle, the extent of conversion which may or may not have used the full NG system potential, and the type of road test over which the exhaust emission check was performed. These data are limited to the standard Otto cycle spark ignition engine; exhaust emission characteristics of other cycles operating with NG or SNG are presently unknown.

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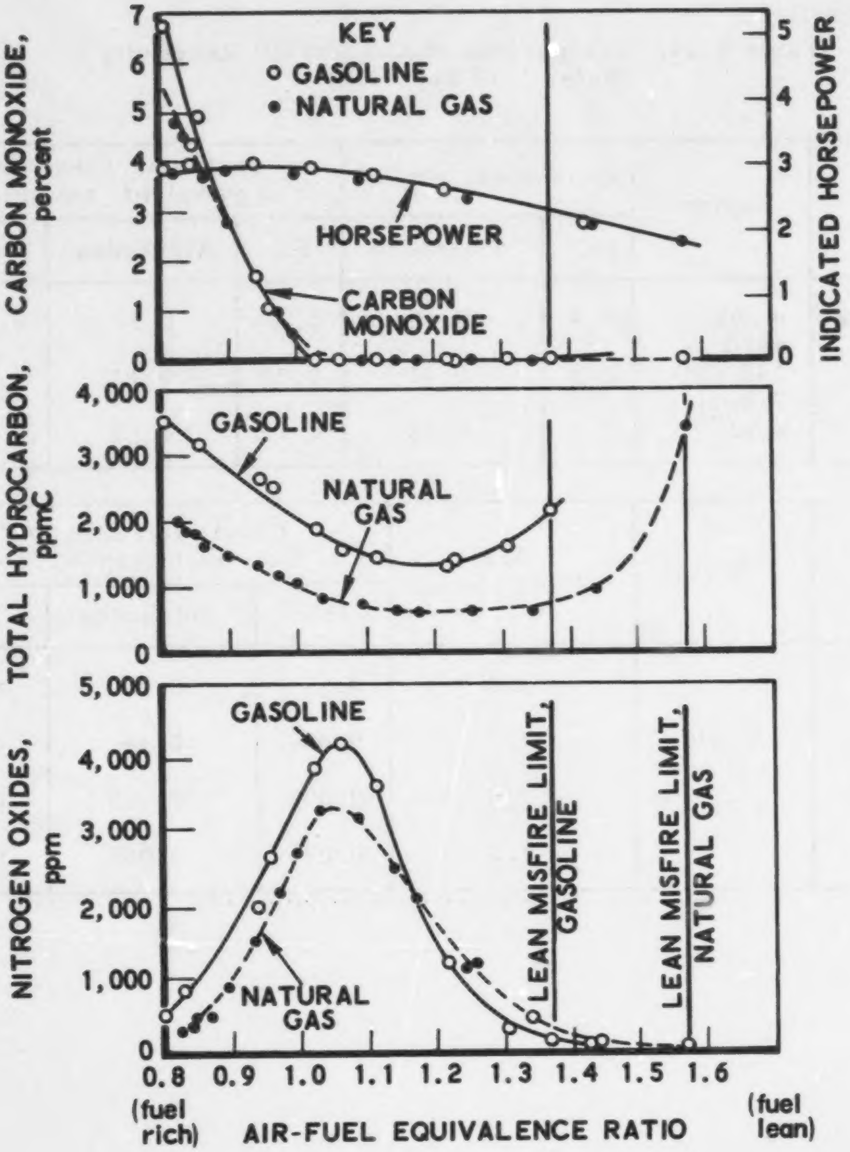
* No taxes, 1971 prices (see Table 5-12). With continually changing 1974 prices, the fuel cost saving will continue to fluctuate.

** For equal Btu expenditure per mile

To provide a firmer basis for the emission characteristics of NG in a spark ignition engine, data for a single cylinder engine (Ref. 5-12) are shown in Figure 5-3. These tests were conducted at the same indicated horsepower for gasoline and NG. The following observations, which are confirmed in all road tests on multicylinder engines including the former seven-mode federal cycle, can be made: the idling carbon monoxide emissions are drastically reduced with NG (as compared to gasoline) because of the possibility of operating at higher equivalence ratios of 1.2 to 1.3 (lean mixtures)with NG; lower HC content with NG because of better mixing and better combustion efficiency; and, finally, lower NO_x content due again to the possibility of operation at air-fuel mixtures leaner than gasoline.

Two factors are not evident in the comparison in Figure 5-3. One is a drop in maximum power when operating a gasoline engine with NG because of a drop in volumetric efficiency of the lower density NG. This drop is approximately 15 percent, as was mentioned before, but it could be partially recouped with a redesigned inlet manifold and higher compression ratios for NG operation. The other factor of importance is the reduced activity of HC emissions with NG as opposed to that of gasoline. Photochemical smog is caused by the action of solar radiation upon inorganic and organic contaminants which include NO_x, HC, and oxygenated HC derivatives. Because HC is the most prominent of organic emissions, it has been given the most attention in estimating smog-forming reactivity of exhaust gas (Ref. 5-12). Reactivity of HC is usually expressed in terms of equivalent ethylene; that is, grams of ethylene having the rate of NO_2 formation equal to that of one gram of organics in the exhaust.

The comparison of reactivity of HC and aldehydes produced in engines run with gasoline, NG, and SNG is shown in Table 5-11.



*Actual Air-Fuel Ratio/Stoichiometric Air-Fuel Ratio - $(\phi)^{-1}$

Figure 5-3. Power and Exhaust Emissions as a Function of Air-Fuel Equivalence Ratio for Gasoline and Natural Gas Fuel (Ref. 5-12)

Table 5-11. Comparison of Exhaust HC Reactivity (Refs. 5-12 and 5-15)

Fuel	Engine	Emissions, gm/mi		Reactivity, Ethylene Equivalent, gm/mi		
		HC	Aldehydes	HC	Aldehydes	Total
Gasoline	8 cyl, 1970 345-CID 7-mode test(20)	4.4	0.19	2.47	0.12	2.59
NG		2.8	0.12	0.30	0.12	0.42
SNG		2.7	0.12	0.13	0.13	0.26

Fuel	Engine	A/F Equivalence	Reactivity, Ethylene Equivalent, gm/ihp-hr		
			HC	Aldehydes	Total
Gasoline	Single cylinder CFR(19)	1.0	0.63	0.09	0.72
		1.2	0.46	0.18	0.64
Natural Gas		1.0	0.092	0.068	0.160
		1.2	0.073	0.088	0.161

As can be seen, the total HC activity with NG is four to six times less than that of gasoline. Further reduction of HC activity is observed with SNG, primarily because of the absence of ethane in SNG. The relatively higher concentration of ethane in NG (in this particular case, 8 percent) against that of SNG (in this case, 0.4 percent) resulted in higher reactive hydrocarbons in the exhaust.

A considerable amount of work was done (Refs. 5-12, 5-15) on the effect of air-fuel ratio and ignition timing on the level of pollutants in the exhaust of NG and SNG fuel in comparison with gasoline-fueled engines. The exhaust sampling technique consisted of a constant volume sampling (CVS) system similar to that described in the Federal Register Vol. 35, No. 136 (Part II, 85, 81) July 15, 1970 . The test cycle on multicylinder engines consisted of the seven-mode federal test cycle beginning with a cold start (Ref. 5-12) and road tests (Ref. 5-15) on a level highway. The engines used were automotive commercial engines of the 1968 to 1970 vintage with a displacement range from 232 to 400 CID. In summary, it was found that with NG operation CO emission was relatively independent on ignition timing and dependent only on air-fuel ratio; that HC emissions were minimum at air-fuel ratio of 19-20, and were decreasing as ignition timing was retarded; and that NO_x values decreased with mixtures leaner than air-fuel ratio of 19 and with retarded ignition timing (Ref. 5-12).

An SNG engine could operate with leaner mixtures than NG before the vehicle performance was degraded. The difference was probably due to improved flame propagation found with the hydrogen-bearing SNG (9.8%). It was also of importance to note the relative insensitivity of NG exhaust emissions to the mileage accumulated and to the ambient temperature changes (Ref. 5-12). Over the 10,000 miles accumulated, the average content in the exhaust of CO (2 gm/mile), HC (1.5 gm/mile) and NO_x (4 gm/mile) remained constant for the vehicles tested. The effect of ambient temperature on exhaust emissions with NG and gasoline is shown in Figure 5-4.

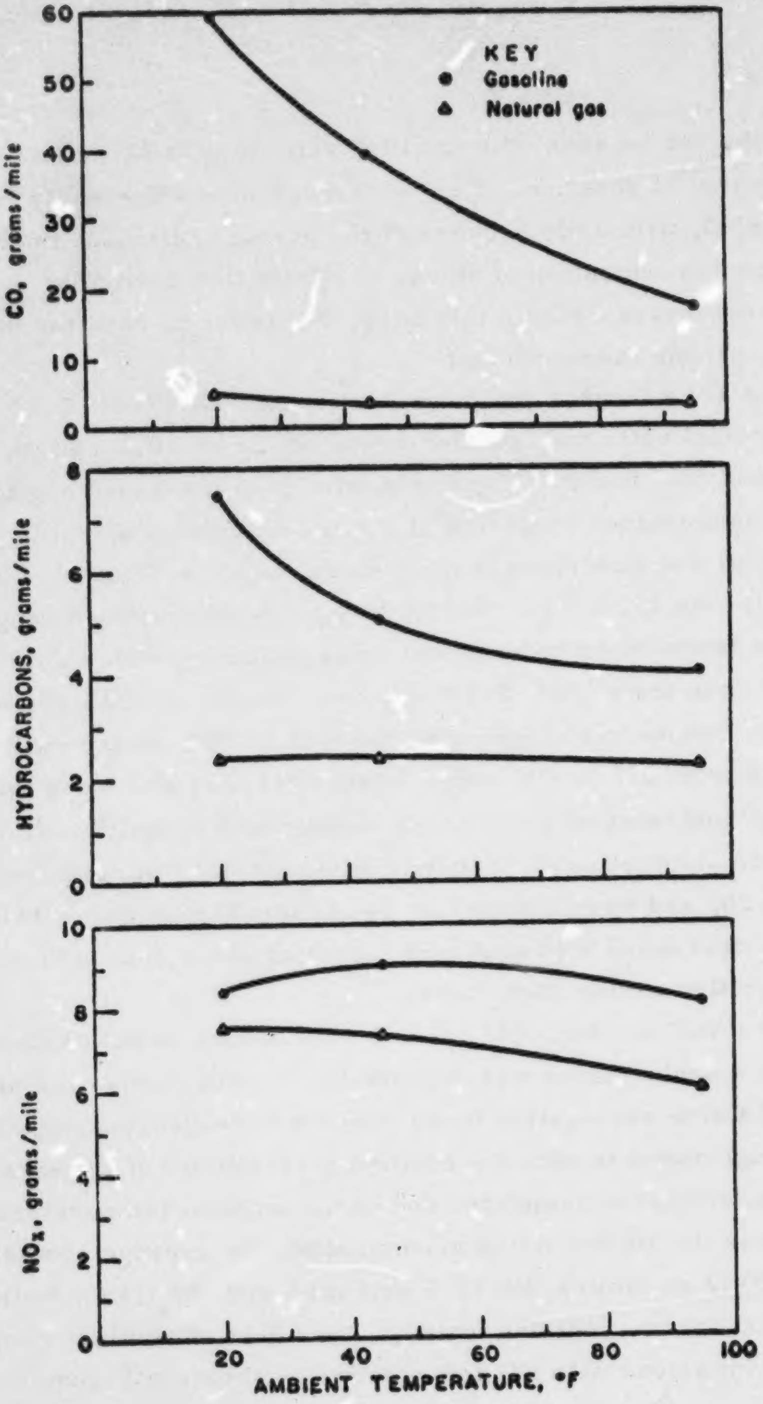


Figure 5-4. Effect of Ambient Temperature on Exhaust Emissions for Gasoline and Natural Gas Fuels (Ref. 5-12)

In a dual-fuel engine operation (gasoline and NG) in which no basic engine changes have been made, a substantial amount of emission data was collected in the former federal seven-mode test cycle on a number of fleet vehicles converted to NG. Both CNG and LNG were used in these tests. Some of the emission data from Reference 5-10 are extracted in the table below.

Summary of Emission Data

Engine Type	Test Condition	CO%		HC, ppm		NO_x, ppm	
		Gasoline	NG	Gasoline	NG	Gasoline	NG
140-200 CID, 1969, 6 cyl	At conversion	2.34	0.09	348	106	855	359
	After 4000 miles	3.21	0.12	378	74	840	359

Approximate conversion to gm/mile for light duty vehicle:

HC - 100 ppm = 1.16 gm/mile
CO - 1% = 21.63 gm/mile
NO_x - 100 ppm = 0.35 gm/mile

A complete conversion to LNG (single-fuel operation) was described (Ref. 5-14) in which the engine compression ratio was increased and other engine modifications were made to take advantage of NG properties. The results of emission test after 50,000 miles are given in the table below.

Emission Test Data (Ref. 5-14)

Emission Type	Car No. 1		Car No. 2	
	Gasoline	LNG	Gasoline	LNG
HC, ppm	175.00	71.00	177.00	90.00
CO %	0.69	0.17	1.06	0.17
NO_x ppm	1655.00	1135.00	1570.00	1277.00

Of interest are emission data obtained on a great number of vehicles by the GSA which are given in Reference 5-9. These data show the familiar emission trend of NG compared to gasoline.

GSA Emission Data (Ref. 5-9)

Emission / Vehicle	HC, gm/mile		CO, gm/mile		NO_x, gm/mile	
	Gasoline	NG[a]	Gasoline	NG	Gasoline	NG
Automobiles	3.13	0.5	41.8	8.6	6.21	2.15
Light Trucks	5.38	1.1	47.2	4.94	3.64	1.79
Medium Trucks	9.83	1.63	65.0	5.96	3.71	2.38

[a] Reduced to 50 percent of measured values to account for reduced reactivity of HC with NG fuel

The emission data for the various alternative engines are limited to use of gasoline only (Ref. 2-1), and these are discussed in Volume II of this report. The reduction of exhaust emissions with NG when compared to gasoline, as shown by the test data, can be expected to occur with other engine cycles because of the possibility of operation on leaner air fuel mixtures, low-activity HC, and a "cleaner" combustion. This expectation must be confirmed by test data.

5.2.5 Toxicity and Safety Effects

The toxicity aspect of methane (or NG) was discussed before, and Table 5-3 indicated that it is less toxic than gasoline and does not present a health problem.

The safety aspects of NG operation (in the form of CNG or LNG) were discussed in the literature by various operators who converted their vehicle fleets to NG. The consensus was that NG may be less hazardous than gasoline because its density is lower than air, which prevents formation of fuel-rich pockets near the ground in case of leakage, and because the ignition temperature of NG is higher (1170°F) than that of gasoline (800 to 900°F). Inspection by insurance underwriters and fire protection officials resulted in acceptance of the conversion vehicles as being as safe or safer than conventional gasoline-powered vehicles.

However, the hazard of operation with NG, and particularly LNG, should not be underestimated. The low boiling point of LNG at atmospheric pressure will require overboard venting when the engine is not operative, and the safe disposal of the boiloff by burning or dissipation in free air must be ensured. This is particularly important for enclosed spaces such as garages, since natural gas can form explosive mixtures with air over a band of air-fuel ratios of 18.0 to 6.2.

Department of Interior regulations presently exist that concern safety valves, fuel tanks, and inspection procedures. The insurance companies are willing to insure CNG or LNG vehicles at nominal rates (i.e., same as gasoline fueled) if properly designed (Ref. 5-9). Special vehicle crush tests with 25 high-pressure CNG bottles were conducted by the Cal-Tech Clean Air Car Project without any bottle failures or even a major displacement (Ref. 5-9).

5.2.6 Handling, Storage, and Distribution Requirements

Storage and distribution of CNG or LNG requires either high-pressure compressors and tanks at the distribution outlet or large cryogenic tanks with appropriate pumping facilities for transfer of the cryogenic LNG to a vehicle tank. Because of the cost of the installation and need for trained personnel, it is unlikely that such equipment would be made available at the 300,000 service stations in the U.S., even if the supply of NG were plentiful. One of the possible solutions to the distribution problem is for operators of fleet vehicles such as GSA, urban transport agencies, utilities, etc., to install their own refueling equipment for CNG or LNG. This is, in fact, the present arrangement for fleet vehicles converted to NG. The other possible solution in the future is to install such refueling equipment only at the major service stations selected on the basis of their large sales volume. The incentive to do that may arise from: (1) a future shortage and rise in cost of gasoline fuel, (2) low cost of NG vehicle operation (lower maintenance cost, lower NG cost, lower taxes), and (3) a continuing effort to achieve and maintain high standards of exhaust cleanliness with minimum sacrifice in fuel consumption. The partial changeover from gasoline to an alternative fuel, such as NG, will not be accomplished rapidly; a period of some five to ten years can be considered a reasonable time. Such a changeover has to be justified not only by the improved operation of the prime mover with an alternative fuel, but also by sound economics for such a changeover, taking into account the overall U.S. picture of energy supply and demand.

5.2.7 Critical Research Gaps

Almost all of the data on automotive engines operating with NG or SNG are limited to spark ignition engines. Even in this case the data are insufficient, and more research is required on engine optimization for NG and SNG to obtain the best compromise between fuel economy and emission level.

With regard to other engine cycles (such as stratified charge engines, diesels, gas turbines, Rankine and Stirling cycles) there are at present no published data on their performance or emission levels with either NG or SNG. This is a research gap which has to be bridged for a future selection of the preferred engine cycle and preferred alternative fuel.

Another gap exists in the hazard assessment of NG and SNG (in the form of compressed or liquefied gas) for its use in automotive vehicles. This includes distribution, vehicle installation, gas storage in confined spaces, and safe disposal of boiloff. Appropriate studies of the problems involved should be made and the necessary regulations issued.

5.3 CURRENT STATUS

5.3.1 Demand

The current production of NG in the U.S. was shown in Table 5-5. Perusal of Table 5-5 shows that import of natural gas in 1970 in the amount of 0.9×10^{12} ft^3 was necessary to meet the growing demand which in the 1960s increased at an average rate of 6 percent per year. Gas utilization in 1971 by sector is shown below. The rate of LNG production in 1970 by U.S.-based plants was 750 million cubic feet per day. However, only a small percentage of NG in the form of either CNG or LNG is currently used for automobiles. It was stated that in 1972 (Ref. 5-13) 3,000 CNG and 500 LNG vehicles were operating in the U.S. These numbers have increased over the last year and are expected to continue to increase in future years; but, in the near term, it will not be a critical factor in the U.S. natural gas energy balance.

1971 Natural Gas Utilization per Sector
Percent of Total Gas Demand

Household and Commercial	Industrial	Transportation	Electrical Generation	Total
32.4	46.0	3.6[a]	18.0	100

[a] Principally power for pipeline gas transportation. (Ref. 1-1)

A decrease in the production of domestic NG is expected in the period 1980 to 1985 and, because production of SNG and the supply of Alaskan gas will not grow fast enough, a larger amount of NG will have to be imported (see Table 5-5).

5.3.2 Consumer Costs

Consumer costs associated with operating an automotive vehicle with NG or SNG in either compressed or liquefied form consist of conversion kit cost (assuming that the customer presently runs a gasoline-powered vehicle), maintenance cost, and fuel cost. The cost of refueling equipment (e.g., compressor or refrigeration units) for CNG or LNG is prorated for amortization purposes in the cost of the fuel, which is shown in Table 5-12. The maintenance costs were discussed briefly before, and it appears that with NG or SNG the maintenance cost of an engine will be reduced by 30 to 35 percent when compared to gasoline.

Table 5-12. Fuel Cost Comparison (Ref. 1-2)
1973 \$ per 10^6 Btu

Cost Item / Fuel	Gasoline (90 Octane)	NG (CNG)	LNG	SNG (Liquefied)
At Terminal	2.15	0.60	1.60	1.50
Distribution	1.00	1.40	1.50	4.00[a]
Total (taxes not included)	3.15	2.00	3.15	5.50

[a] Includes liquefaction cost.

There is a possibility of fuel energy saving when operating a vehicle on SNG or NG as compared to gasoline, but for the purpose of cost comparison equal Btus utilization is assumed.

The conversion cost will depend on the CNG or LNG tank size and on the number of vehicles converted. Estimates given by fleet operators varied between $300 to $500 per vehicle (the higher figure for LNG).

The economics of complete conversion will become more attractive with the rising cost of fuel. Assuming a fuel saving cost of $125 per year, as shown in Section 5.2.3, and assuming a maintenance saving of 0.15 cents per mile, based on data in Reference 5-9, a total annual saving of $142 will result. The cost of the conversion kit would then be amortized in 2-1/2 to 3 years at 1971 prices. In the current rapidly fluctuating fuel price market, however, this type of tradeoff analysis must be reviewed on a continual basis, particularly if government price regulations are relaxed or eliminated. Furthermore, since SNG would ultimately have to be used, because of limited NG supplies, the higher-priced SNG would be competitive only at the time when gasoline prices have risen substantially above the figures cited for 1971.

5.4 PROJECTED STATUS

5.4.1 Availability

5.4.1.1 Near Term (1975 to 1985)

The availability of NG and SNG in the 1975 to 1985 time period was discussed briefly before and was presented in Table 5-5, which indicated the growing need for NG/LNG imports and the beginning of SNG, albeit in small quantities, in 1980. Projected figures for SNG differ from different references. A projection from Reference 5-7, for example, is given in Table 5-13 showing SNG production volumes, both from coal and petroleum liquids, larger than those predicted (Refs. 1-1 or 5-2). Projections for Case I (Ref. 5-2) are 2.3 percent of total domestic supply in 1980,

Table 5-13. Comparison of U.S. Energy Forecasts by the Bureau of Mines and Institute of Gas Technology (IGT)(Refs. 1-1 and 5-7)

	1985		2000	
	Bureau of Mines	IGT	Bureau of Mines	IGT
Total Primary Energy Consumption, quadrillion (10^{15}) Btu	116.6	125.2	191.9	228.2
Source, percent				
Petroleum	42.6	43.1	36.2	32.8
Shale Oil	0.9	0.5	1.0	2.8
Coal	18.4	18.9	16.3	24.6
Dry Natural Gas	24.3	17.5	17.7	11.1
Nuclear Energy	10.1	16.8	25.7	26.3
Hydro and Geothermal Energy	3.7	3.2	3.1	2.4
Oil Supply				
Total, million bbl/day	25.0	26.9	35.5	43.0
Sources, percent				
Total Domestic U.S. Petroleum Liquids, Excl. North Slope	36.8	36.1	16.9	18.6
Total North Slope Liquids	8.0	7.4	10.0	7.0
Shale Oil	2.0	1.1	2.8	7.0
Syncrude from Coal	--	0.7	--	9.3
Net Imports	53.2[a]	54.7	70.3[a]	58.1
Gas Supply				
Total, trillion cu ft/year	29.537	25.6	38.459	35.3
Sources, percent				
Lower 48 Production	73.9	67.2	57.6	37.4
Alaska		5.9		12.7
Net Pipeline Imports	13.9	9.8	19.3	15.6
Net LNG Imports	5.4	6.2	8.8	8.8
Syngas from Petroleum Liquids	6.8	6.6	14.3	2.3
Syngas from Coal		4.3		23.2
Coal Consumption				
Total, million tons/year	980	1028	1418	2333
End Use, percent				
Conventional	82.3	79.8	70.7	54.4
Syngas	8.8	6.4	21.7	21.1
Syncrude	--	1.8	--	16.3
Exports	8.9	12.0	7.6	8.2

[a] Based on present trends and policies; may include additional domestic supplies from conventional sources or from synthetics, depending on governmental policies, environmental restraints, economic conditions, and technological developments.

7.3 percent in 1985. Reference 1-1 predictions for the same period are three percent and 8.4 percent, respectively. With imports removed from supply figures, Reference 5-7 predicts SNG production of 12.9 percent of total domestic gas in 1985. Reference 1-2 provides a more detailed forecast of SNG production through the year 2000, and the data are shown in Table 5-14. The Hi-Btu Syngas data are in reasonable agreement with IGT forecasts shown in Table 5-13. However, even with optimistic projections for SNG, only NG either in the form of CNG or LNG would be considered as an alternative fuel in the near-term period.

Industrial and electricity generation users now rely on a mix of coal, liquid petroleum, and natural gas fuels. A small increase in the percentage of coal used by these consumers would make sufficient NG available for future growth in transportation needs. However, the application of NG in the transportation sector may be limited not so much by the gas supply in the near-term period as by other inhibiting factors, such as distribution and storability.

Summarizing the comments it can be stated that, in addition to other fuels discussed in the report, NG in the form of CNG or LNG cannot be considered a viable candidate for alternative fuels on a large scale within the near-term period.

5.4.1.2 Far Term (1985 to 2000)

In the far term, development of advanced engine cycles are expected to be completed, and the most efficient engine may be available in mass production.

SNG as an alternative fuel will be of significance since, as noted previously, 20 to 25 percent of the total gas supply will come from coal gasification (see Tables 5-5 and 5-13). The most probable SNG use would be in stationary power plants, thus releasing more of the liquid fuels for transportation use. Gas from oils is not likely to be of importance, even in this time period, with estimates of only 2.3 percent of the gas supply coming from liquid petroleum. (See Table 5-13.)

Table 5-14. Plausible Schedule for Buildup of Coal Syngas Production (Ref. 1-2)

Year	Annual Production, TCF			Coal Required Million ST[b]
	Hi-Btu	Lo-Btu[a]	Total	
1978	0.08	-	0.08	5
1981	0.4	0.2	0.6	37
1982	0.55	0.25	0.8	48
1983	0.7	0.4	1.1	62
1984	0.9	0.6	1.5	91
1985	1.1	0.8	1.9	115
1986	1.3	1.1	2.4	195
1990	2.4	2.3	4.7	235
1995	4.1	4.2	8.3	500
2000	5.6	6.0	11.6	700

[a] Lo-Btu gas reported in terms of Hi-Btu gas equivalency, i.e., corrected to a heat content of 1000 Btu/CF.

[b] In terms of bituminous coal. Corresponding tonnages of subbituminous coal or lignite would be higher because of the lower Btu contents of these lower rank coals. Tonnages may be overstated because of the lower amount of process energy required to make Lo-Btu gas, i.e., by not having to use energy for the methanation step required in the production of Hi-Btu gas. On the other hand, the conversion of Lo-Btu gas to methanol does have an energy requirement and, to the extent that the end product is methanol rather than Lo-Btu gas, the coal requirement on the basis of product Btu content would approach that of Hi-Btu gas production.

5.4.2 Projected Consumer Cost

The projected cost of NG in 1970 dollars is shown in Table 5-15. These figures represent an average "required cost" at the well-head to obtain a 15-percent Return on Investment (ROI). Depending on the rate of investment and the discovery rate, the 1985 prices per thousand cubic feet will be higher compared to 1971 prices by a factor of 1.6 to 2.3.

It has to be pointed out that the cost projections in (Refs. 1-1, 5-2, 5-7, and others) were made without an assumption of steep increases in prices of petroleum products, and of higher rates of inflation such as are taking place in the 1973 to 1974 period. Consequently, the figures quoted in this Section will require an upward revision, if the increased inflationary trend continues into the 1975 period and beyond.

The SNG cost of $\$1.50/10^6$ Btu at the refinery (See Table 5-12) was quoted for the post-1985 period. These costs will vary comparatively little with the various processes and will depend mainly on the cost of raw material, that is, coal. The formula for derivation of the cost of SNG in 1971 dollars, f.o.b. mine, is based on data from IGT (Ref. 5-17):

- SNG cost ($\$/10^6$ Btu) = coal cost ($/ton) × 0.16 + 0.7.

The projected cost of surface coal, which is of primary interest in the coal gasification process, is shown in Figure 5-5. The consumer cost of SNG (no taxes, 1973 dollars) is also shown in Table 5-12.

Thus for a $5 per ton cost of coal, the cost of SNG is $\$1.50/10^6$ Btu; for $7 per ton cost of coal, cost of SNG would be $\$1.80/10^6$ Btu.

Further cost increases for NG and SNG could be extrapolated into the 1985 to 2000 far-term period, but there were no data available in the literature to support such an extrapolation. However, assuming speculatively an annual 5 percent inflation rate between 1985 and the year 2000, and 3 percent increase in mining cost because of the accessibility and depth of gas deposits, the manufacturing cost of NG shown in Table 5-15 for 1985 could be increased

Table 5-15. Required Natural Gas Field Price in 1970 Constant Dollars at 15% Return on Net Fixed Assets (Excluding Alaska)

National Petroleum Council - 1972

(Ref. 5-2)

	Cents/MCF			
	Case I	Case II	Case III	Case IV
Drilling Rate	High Growth	Medium Growth	Medium Growth	Current Downtrend
Finding Rate	High	High	Low	Low
1970 (Actual)	17.1	17.1	17.1	17.1
1971	23.5	23.5	23.5	23.5
1975	26.7	26.2	27.9	26.6
1980	33.7	31.8	37.8	31.6
1985	43.6	39.8	53.0	38.7

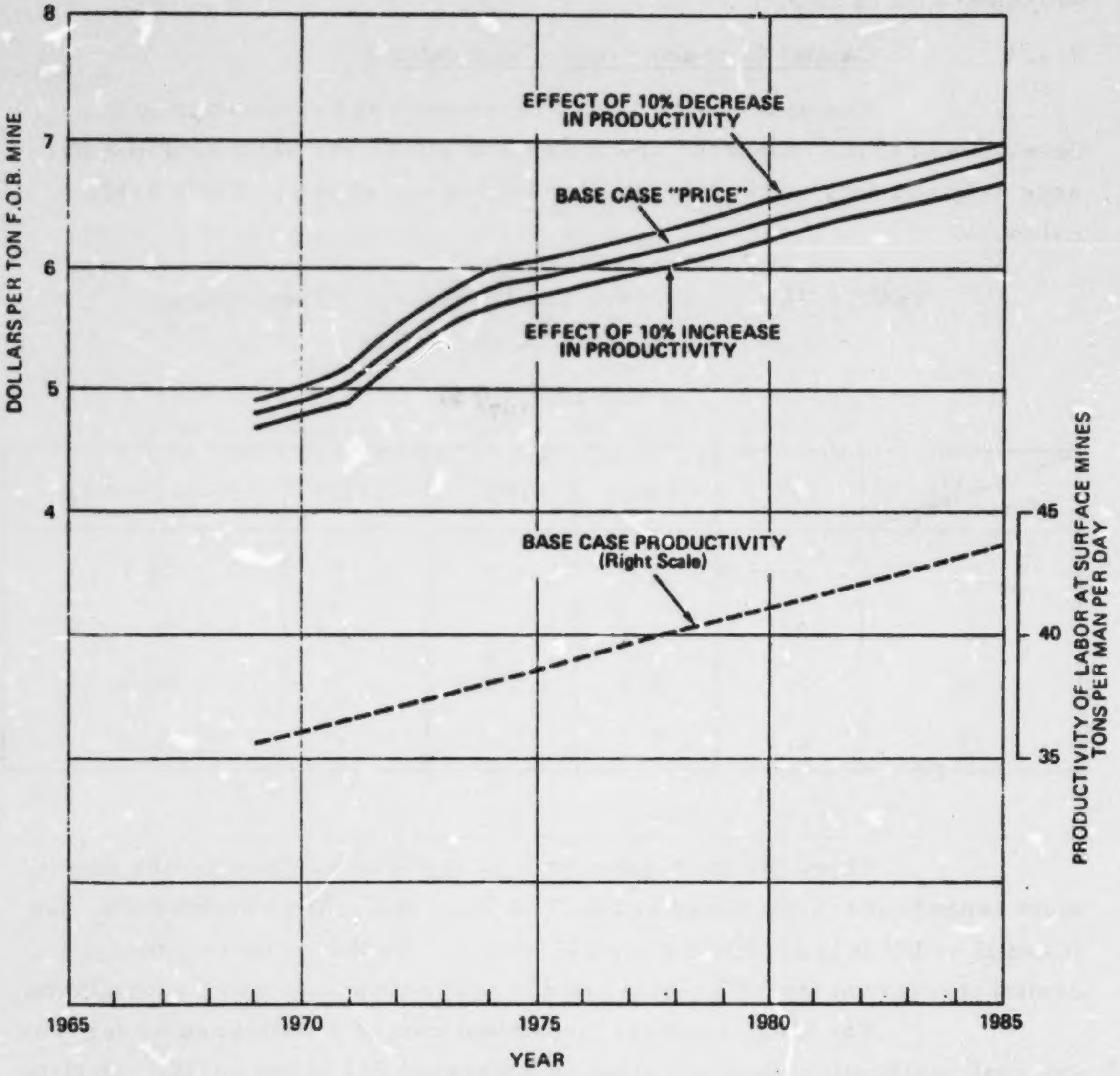


Figure 5-5. Effect of Productivity on the Average Value of Coal From Surface Mines (Constant 1970 dollars - 15% of Return, 3% growth rate) (Ref. 5-2)

by a factor of 2 for the year 2000. Similar reasoning could be applied to the projected cost of SNG.

5.4.3 Capital Cost and Timing Implications

The cost of both capital investment and exploration in the development of NG resources and production plants was estimated in Reference 5-2, and data extracted from that source are shown in Table 5-16, below.

Table 5-16. Exploration and Development Expenditures
for NG in U.S. (Ref. 5-2)
(billion 1970 $)

Year / Case	1971	1975	1980	1985	15-year Total
I	2.1	2.7	4.6	5.8	58.7
II	2.1	2.4	3.6	4.3	47.1
III	2.1	2.4	3.6	4.3	46.3
IV	2.0	1.8	1.7	1.5	26.5

Thus, for the highest rate of exploration (Case I), the investment expenditure is predicted at $58.7 billion, and at the intermediate case (Case II or III) it is approximately $47 billion. To this must be added the capital investment for SNG plants and for coal mines supporting such plants.

For SNG, a typical investment cost of a million cubic feet per day coal gasification plant are given in Reference 5-1 based on El Paso Natural Gas Company estimates. Cost for water supply lines, reservoir, etc. for the plant itself would cost approximately $40 million. Process modifications needed to meet stringent sulfur emission restrictions and other environmental requirements total, perhaps, an additional $60 million. A reasonable approximation of plant cost itself based on these data is $1 to $1.2 per cubic foot per day.

The estimated implementation schedule for production coal gasification plants is shown in Table 5-17. The output of 40 plants in 1990 will correspond to approximately $3.2 \times 10^{12} ft^3$ per year, which is in reasonable agreement with projections in Table 5-5.

The cumulative investment cost of these plants is estimated to be approximately $10 to $12 billion. The plants are expected to consume approximately 2.6×10^8 (Ref. 5-1) tons/year of coal in 1990 at a minimum capital approximately $3 billion for water supply (for cooling and steam) and other facilities and perhaps $2 billion for environmental control, with a total of approximately $20 to $21 billion. This figure is close enough to the $25 billion quoted in Reference 5-16 for coal-associated synthetic gas and crude projects by 1990. Such investment funds may be difficult to raise in light of the energy industry's high risks associated with new processes and plants, and there may be need for governmental subsidy or for participation of the oil-producing nations themselves (Ref. 5-16).

5.4.4 Impact with Other U.S. Energy Requirements

The transportation sector has to compete in the gas and liquid petroleum products with the household, commercial, industrial, and electrical generation sectors. Since it appears that in the near-term and possibly even in the far-term period, energy for the transportation sector will be mostly based on petroleum fuels, it is necessary to examine the other sectors, mainly the industrial and electric generation, for possible use of coal or nuclear fuels to relieve demand on petroleum fuels.

From the general review of the energy resources in the Introduction Section, it appears that competitive demand for liquid petroleum and NG will exist through the year 2000. Some easement in that shortage in self sufficiency of the United States could be realized by an accelerated program of coal mining and more rapid conversion of the industrial and electrical sectors toward coal, as well as utilization of electrical energy for automotive application in the far-term period.

Table 5-17. Cumulative Number of 250 Million Cubic Feet/Stream Day Coal Gasification Plants (Ref. 5-7)

Year	77	78	79	80	81	82	83	84	85	90
Lurgi	1	1	2	2	3	3	4	5	6	6
New Process A	.	.	.	.	1	1	2	3	4	14
New Process B	.	.	.	.	.	1	1	2	2	4
New Process C	.	.	.	.	.	.	1	1	2	16
Total	1	1	2	2	4	5	8	11	14	40

5.4.5 Factors Which May Inhibit Use

One of the major problems in the widespread use of an alternative fuel such as NG or SNG is the distribution system. There are at present approximately 300,000 service stations and 300 terminal outlets in the U.S. for distribution of gasoline. The investment in station refueling equipment for CNG is approximately $25,000 and for LNG $50,000. It is apparent that such an investment at a service station has to be justified on the basis of economics. It could possibly be considered for major stations with large sales volume if the number of vehicles on the road equipped with CNG or LNG conversion kits is large enough to guarantee a return on the investment. The number of CNG or LNG vehicles will, in turn, depend on the economy of operation whereby the user must be convinced of safe operation, good fuel economy, and less costly maintenance. Considering these factors, it appears that in the near- and probably the far-term, the use of NG will be limited mainly to fleet vehicle operation with their own depot refueling. Experience obtained in operation of such vehicles, and well proven fuel and maintenance economy, may be a factor in gradual proliferation of its use, particularly if the prospect for future supply of NG and SNG appear favorable. For the year 2000, this combination, combined with possible severe limitation of liquid petroleum imports in the future, may force the contribution of NG or SNG powered vehicles from the predicted 6.1 percent to greater than 12 percent, based on the prediction of Reference 5-7.

5.4.6 Critical Technology Gaps

The technology gaps existing in the application of NG or SNG to automotive vehicles have already been discussed.

The technology in coal gasification is well founded, and funding is being accelerated to bring the various processes into the production stage.

The environmental problems connected with large-scale surface coal mining, previously discussed, remain to be solved. The large investment funds for continuing NG exploration and production, as well as funds for large-scale operation of coal gasification plants, must be planned well in advance of need.

The vehicle storage tanks for liquified NG or SNG require insulation improvements for reducing their bulk and weight. The quality of the insulation and tank suspension should be aimed at minimizing the boiloff to one percent per day.

Safety aspects of the storage and use of compressed or liquid gas in automotive vehicles must be covered by appropriate regulations which must be developed.

5.4.7 Potential for National and Regional Transportation Use

The potential for NG and later for SNG-powered vehicles is good for regional transportation use and fleet vehicle operation, but the national use will be inhibited by the need for a costly distribution system. The possibility of conversion and operation of a large number of vehicles from selected refueling points for fleet operation reduces the cost of conversion equipment and leads to early amortication of the investment. A possible saving in fuel energy of approximately 20 percent, as compared to 1976 spark ignition gasoline engines equipped with emission control devices, and lower maintenance cost will be additional factors favoring such a conversion. The fuel economy of NG or SNG will result mainly from its characteristic high octane number (> 105) permitting operation of engines at higher compression ratios, advanced ignition timing and lean mixtures, while the unleaded gasoline coming into use require reduced compression ratios and retarded ignition.

SECTION 6

PROPANE AND BUTANE

Propane and butane are variously known as LP-gas (liquid petroleum gas), bottled gas, or tank gas. LP-gas actually consists of various petroleum-associated chemical compounds whose boiling temperatures are below normal room temperature but above those of the constituents of natural gas (i.e., methane and ethane). LP-gas comprises several of the aliphatic hydrocarbons, such as propane, propylene, butane, butylene and butadiene. The principal commercial products are propane and butane, and, because of the chemical and physical properties of these compounds (higher octane rating and other desirable characteristics), they are the only potential LP-gas candidates considered in this study as alternative automobile fuels.

6.1 CHARACTERIZATION

6.1.1 Chemical Composition

Propane and butane belong to the saturated paraffin hydrocarbon group, having the general chemical formula, C_nH_{2n+2}, where n is the number of carbon atoms. Propane, C_3H_8, exists in but one chemical structural form, while butane, C_4H_{10}, can exist in one of two isomeric forms (i.e., as n-butane or isobutane).

6.1.2 Physical Properties

Both propane and butane are gaseous hydrocarbon fuels under ambient conditions, having boiling points of -44°F and 31°F respectively at atmospheric pressure. Thus, they are more volatile (lower boiling temperature) than gasoline mixtures but are less volatile than natural gas. Consequently, they can be stored easily in a liquified state by either pressurizing the storage container or cooling them below their relatively moderate boiling points. Of the two, propane is more generally suitable for on-the-road automotive vehicles because of its lower boiling point and higher octane rating.

The lower boiling point of propane permits its use in colder climates, where butane may require a separate heating source to vaporize the fuel for initial engine starting. Propane does, however, require higher tank storage pressures than butane to maintain it in a liquid state, but these pressures are still very moderate for pressurized systems and do not present any difficulties.

Propane and butane are both odorless and colorless gases; consequently they require the addition of a strong-smelling additive to enable the user to detect leaks. Pertinent physical properties are listed in Table 6-1 for both pure and commercially delivered products (Ref. 6-1). Important characteristics for automotive fuels are the higher heating value (heat of combustion), combustion temperature and the octane number. These characteristics for propane, butane, and gasoline are compared in the following table.

	Propane*	Butane*	Gasoline
Net Heating Value			
Btu per Pound	19,950	19,700	19,080
Btu per Gallon	85,000	96,000	117,000
Combustion Temp. °F	3,595	3,615	3,700
Motor Octane	96	89	83-95

This table indicates that propane, butane, and gasoline are generally comparable as fuels. In terms of higher heating value, propane and butane are higher than gasoline on a weight basis but lower on a volume basis (gasoline has a higher density).

6.1.3 Sources and Domestic Reserves

The principal sources of LP-gas are (1) crude-oil wells, (2) natural gas wells, (3) light hydrocarbon gas wells, and (4) refinery operations. In all of these sources, LP-gas is generally a by-product of derivation or production of natural gas and gasoline. The LP-gas domestic reserves are therefore related to the domestic crude oil and natural gas reserves.

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*Propane and butane properties are for average commercial products.

Table 6-1. Physical Properties of Propane and Butane (Ref. 6-1)

Physical Properties	Propane		Butane	
	Pure	Commercial	Pure	Commercial
Vapor Pressure, psig @ 70°F		124		31
@ 100°F		192		59
@ 130°F		286		97
Specific Gravity of Liquid @ 60/60°F	0.51	0.509	0.584	0.582
Initial Boiling Point @ 14.7 psia, °F	-44	-51	31	15
Weight Per Gal. of Liquid @ 60°F, lb		4.24		4.84
Specific Heat of Liquid @ 60°F, Btu/lb°F		0.588		0.549
Cu Ft of Gas @ 60°F, 30" Hg, per gal liq @ 60°F		36.28		31.46
Spec. Vol of Gas, @ 60°F, 30" Hg, cu ft/lb		8.55		6.50
Spec. Heat of Gas @ 60°F(Cp), Btu/lb°F		0.404		0.382
Spec. Grav. of Gas (Air = 1) @ 60°F, 30" Hg.	1.56	1.52	2.01	2.01
Ignition Temp. in Air, °F	808	920-1,020		900-1,000
Max. Flame Temp. in Air, °F	3,573	3,595		3,615
% Gas in Air for Max. Flame Temp.		4.2-4.5		3.3-3.4
Max. Rate of Flame Propagation in 25 mm Tube, in/sec.		33.4		34.3
Limits of Flammability, % gas in air	--	--	--	--
@ Lower Limit		2.4		1.9
@ Upper Limit		9.6		8.6
Required for Complete Combustion, lb air/lb gas	15.70	15.58		15.3
Latent Heat of Vaporization @ Boiling Point				
Btu/lb		185		167
Btu/gal		785		808
Total Heating Values (after vaporization)	--	--	--	--
Btu/lb	21,661	21,560	21,134	21,180
Btu/gal		91,500		102,600
Btu/cu ft	2,580	2,522		3,261

Notes: 1. The physical properties of commercial propane and butane can vary widely depending on the varying amount of impurities included.

2. Commercial properties obtained from Petroleum Processing Handbook by Bland and Davidson, McGraw Hill Book Company.

Proven reserves of natural gas liquid at the end of 1970 were about 7.7 billion barrels (Ref. 6-2). These natural gas liquids are composed of LP gases and ethane, natural gasoline and isopentane, and other products. Liquified petroleum gas accounts for slightly over one half of these natural gas liquids. Considering a current domestic use rate of gasoline of approximately 80 billion gallons per year, the total LP-gas reserves would last about one year if used exclusively as an automotive fuel.

6.1.4 Manufacturing Methods

The primary production of LP-gas (approximately 74 percent of total production) comes from natural gas processing. LP-gas is recovered from natural gas by three basic recovery methods: compression, adsorption, and absorption. The most common process for recovery of LP-gas and natural gasoline liquids from natural gas is the oil absorption process. A simplified flow diagram for a typical oil absorption process is shown in Figure 6-1. (Ref. 6-3).

The natural-gas feed exchanges heat with the residue gas from the overhead of the absorber followed by further cooling by refrigeration to about -35°F. It is then dried by means of diethylene or triethylene glycol, which is injected into the gas feed ahead of the cooler. The gas from the cooler enters a glycol separator where glycol containing water is separated from the natural gas as a liquid phase from which, by distilling off the water, a dry glycol is recovered for recycle to the injection. The gas and any hydrocarbon condensate passes to the base of the absorber, where it is contacted with absorption oil at -35°F entering at the top of the absorber. About 85 percent of the propane and essentially all of the higher-boiling hydrocarbons are absorbed in the oil. The overhead residue gas from the absorber, at about -15°F, is heat-exchanged with the inlet gas after which, at 40°F and 600 psig, it flows to the booster where the pressure is increased to that of the natural gas line.

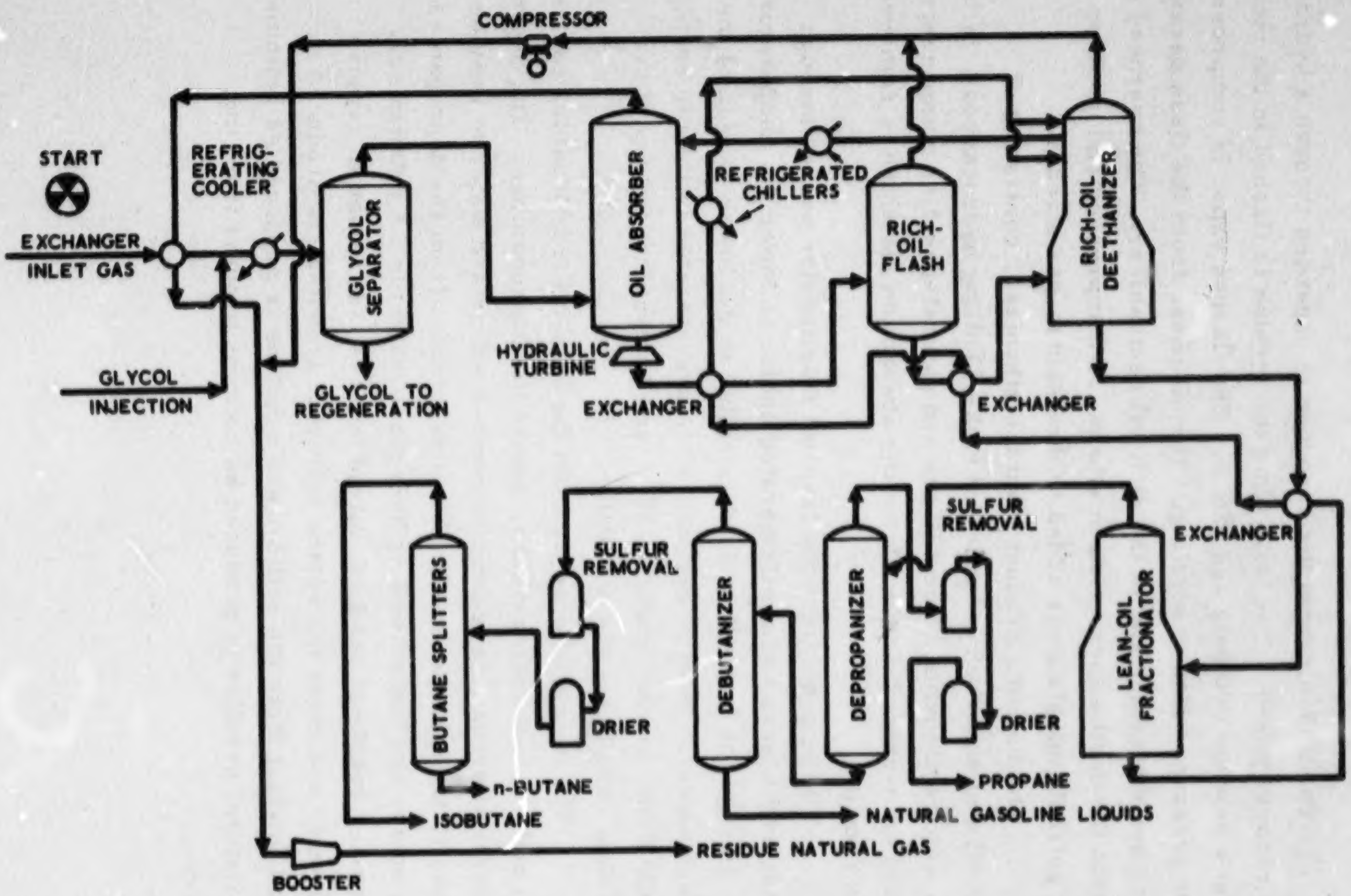

COMPRESSOR
START
REFRIG-ERATING COOLER
EXCHANGER
INLET GAS
GLYCOL INJECTION
GLYCOL SEPARATOR
GLYCOL TO REGENERATION
OIL ABSORBER
HYDRAULIC TURBINE
EXCHANGER
REFRIGERATED CHILLERS
RICH-OIL FLASH
EXCHANGER
RICH-OIL DEETHANIZER
EXCHANGER
LEAN-OIL FRACTIONATOR
SULFUR REMOVAL
DRIER
DEPROPANIZER
PROPANE
DEBUTANIZER
NATURAL GASOLINE LIQUIDS
SULFUR REMOVAL
DRIER
BUTANE SPLITTERS
n-BUTANE
ISOBUTANE
BOOSTER
RESIDUE NATURAL GAS

Figure 6-1. Refrigerated Absorption Process for the Production of LP Gas and Natural Gasoline Liquids (Ref. 6-3)

The rich oil from the absorber is expanded through a hydraulic turbine to recover power. The fluid from the turbine is flashed in the rich-oil flash tank to about 300 psig and -26°F. The flashed vapor is compressed to the inlet pressure before recycling. The oil phase from the flash passes through another exchanger and to the rich-oil deethanizer. The overhead gas product from the deethanizer, rich in ethane, is compressed and used for producing petrochemicals or is added to the residue-gas stream.

The bottoms product from the ethanizer, consisting of absorption oil and absorbed propane and higher-boiling hydrocarbons, is fed to the lean-oil fractionator. The LP-gas and natural-gasoline components are removed as overhead product from the absorption oil which is removed as bottoms product.

The lean oil from the lean-oil fractionator passes through several heat exchangers and a refrigerated cooler to lower the temperature to -35°F. Part of the lean oil is used as reflux to the lower section of the rich-oil deethanizer. Most of the lean oil is presaturated in the top section of the deethanizer, cooled again to -35°F and returned to the top of the absorber, thus completing the oil cycle.

The overhead product from the lean-oil fractionator, consisting of propane and heavier hydrocarbons, enters the depropanizer. The depropanizer overhead product is treated to remove sulfur and water to provide LP-gas specification propane. The bottoms product from the depropanizer containing butane and higher boiling hydrocarbons enter the debutanizer. The debutanizer overhead product, mixed butanes, is treated to remove sulfur and water and enter the butane splitter. Isobutane is produced as an overhead product from the splitter and n-butane is produced as bottoms product. Natural gasoline is produced as bottoms product from the debutanizer.

6.2 SUITABILITY FOR USE AS AN ENGINE FUEL

6.2.1 Engine/Vehicle Compatibility

The use of LP-gas as an internal combustion engine fuel has a long history, dating back to the early 1930s. The early commercial product was an uncertain mixture of propane, butane, and other gases with variable chemical and physical properties. Its use as an engine fuel resulted in many problems, leading to disagreements as to its advantages and disadvantages. Some of the early problems involved frozen fuel lines, hard starting, clogging filters, oil contaminants in LP-gas, blown head gaskets, burned valves, scored pistons, broken rings, etc. Many of these problems were attributed to the variations in constituent gases incorporated in the commercially available product. Also, the use of mixtures high in butane resulted in some further difficulties when operated in cold climates; e.g., vaporizing the fuel during engine starting, due to the relatively high condensation temperature of butane (31°F). In order to solve these problems by obtaining a more standardized product, the National Gas Processors Association (in 1962) adopted a specification for a propane engine fuel, which was designated HD-5. This engine has a minimum of 90 percent propane, a maximum of 5 percent propylene, and meets certain other standards of purity. The following discussion on the suitability of liquefied petroleum gas as an engine fuel refers to HD-5 or higher grades of propane.

Propane appears suitable for use in all of the alternative engines currently being considered. For the conventional reciprocating spark ignition engine, operation with propane involves several differences from operation with gasoline. The required propane equipment consists of:

a. A pressurized tank to contain propane as a liquid (with a working pressure of 250 psig, and weighing about 80 pounds for a tank capacity of 20 gallons)

b. A regulator/convertor with the dual functions of vaporizing the fuel from liquid to a gas and of regulating the gas pressure to the propane "carburetor"

c. An automatically controlled shutoff valve that positively stops the flow of fuel when the engine is not in operation

d. A propane "carburetor" or device for mixing gaseous fuel and air

e. Excess pressure-relief valves in the tank and in some installations between the tank and shutoff valve and engine to avoid potential overpressure conditions. The pressure-relief valves are connected to a high level vent pipe. These items replace the atmospheric-pressure fuel tank, fuel pump, and carburetor of a gasoline-operated engine. The modification involved in operating other engine candidates on propane are not defined at this time, but they are not expected to be significantly different from those indicated for the conventional reciprocating spark ignition engine.

6.2.2 Fuel Economy Effects

In general, the use of gaseous fuels will provide for better mixing of the fuel-air charge, particularly in multicylinder engines where uniform distribution of the mixture from cylinder to cylinder and within each combustion chamber is difficult to achieve. This permits leaner mixtures to be used, which may result in some measurable gain in specific fuel consumption. Additionally, for the spark ignition engine, the high octane rating of propane permits a higher compression ratio to be used in the design, thereby improving the thermal efficiency and, accordingly, specific fuel consumption characteristics of the engine. It should be noted, however, that the current trend in automotive engine design is toward lower compression ratios to minimize the production of NO_x.

The overall improvement in fuel economy attainable through the use of propane in different engines is difficult to predict. For the conventional spark ignition engine, different users have experienced varying results, depending on the condition of the engine, weight of the vehicles, air-fuel mixture ratio, engine power setting, and a host of other variables. Reference 6-4, for example, indicates a reduced specific fuel consumption (SFC) of 13 percent by using propane instead of gasoline.

6.2.3 Emission Effects

Use of propane as an automotive fuel minimizes the problem of controlling evaporative HC emissions in conventional reciprocating engines, since the storage and supply systems are pressurized. Venting will occur only during excessively high operating and storage temperature conditions, when the propane is vented through one or more pressure-relief valves. Usually, a single valve located in the fuel tank is provided. The problem of liquid evaporation, as from a gasoline carburetor, is nonexistent. In any of the engine candidates under consideration, the use of a fuel introduced as a gas tends to promote even mixing and thereby enhances combustion, permitting leaner mixtures to be used without significant loss in engine performance or response. Leaner mixtures tend to reduce HC, CO, and (at very lean mixture ratios) NO_x emissions. Further, the reactivity of the exhaust products (tendency to react with sunlight to form photochemical smog) is reduced when burning propane, as the exhaust products contain a smaller fraction of reactive olefins than the exhaust products of gasoline-like fuels.

For the conventional internal combustion engine, the reduction in emissions using propane instead of gasoline has been measured by a number of investigators. However, test data based on the use of the 1972 or 1975 federal certification test procedures are limited, and these data are largely comprised of tests on older model year cars. Table 6-2 summarizes some of the available emission test results for propane versus gasoline as used in conventional engines (Ref. 6-5). It will be noted that in a few instances one or more of the measured pollutants showed an increase in emission levels when propane was used. However, the bulk of the data shows that substantial reductions in exhaust HC, CO, and NO_x are concurrently achievable by the use of propane fuel.

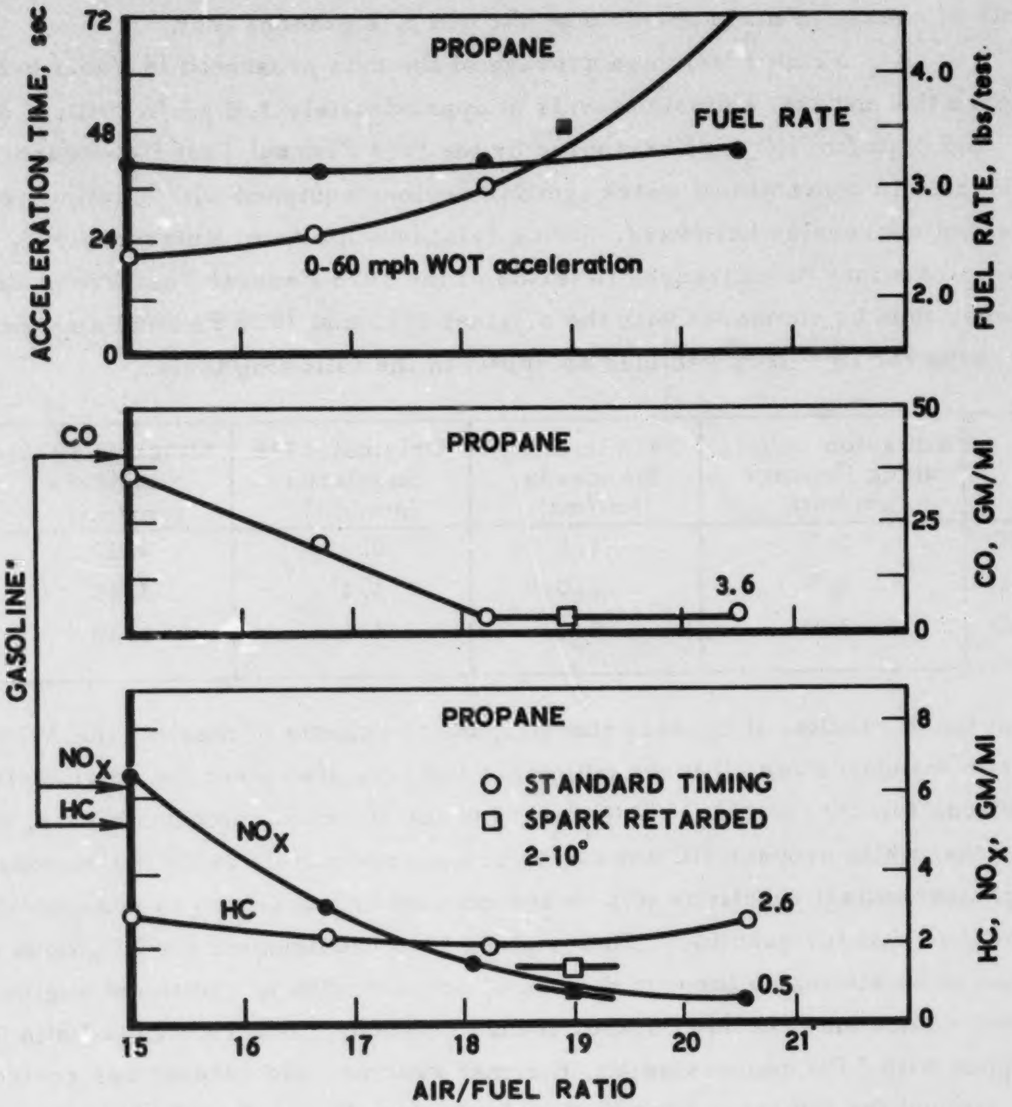
Much of the variability in the data shown in Table 6-2 is undoubtedly due to variations in the engine settings for air-fuel ratio and spark timing. The influence of these factors on emission levels and the potential for operating at extremely lean mixtures with propane fuel are

Table 6-2. Typical Emission Reduction through Gaseous Fuel Conversion (Fig. 6-5)

Vehicle	1972 FTP Emissions (grams/mile)			Type Conversion
	HC	CO	NO_x	
Converted 1968 Buick 350	3.5	4.7	8.9	LPG
Stock 1968 Buick 350	1.9	29.6	4.0	
Percent Reduction	(84)*	84	(123)*	
Converted 1969 Ford 351	3.1	7.3	8.6	LPG dual fuel
Stock 1969 Ford 351	7.4	17.8	5.2	
Percent Reduction	58	59	(65)*	
Converted 1968 Ford 302	2.4	4.2	1.8	LPG dual fuel
Stock 1968 Ford 302	3.1	28.5	3.6	
Percent Reduction	23	85	50	
4 Converted 1969 Chrysler 318s	2.4	7.2	2.9	LPG dual fuel
Stock 1969 Chrysler 318	3.4	30.5	3.6	
Percent Reduction	29	76	19	
2 Converted Rambler 343s	3.0	15.4	2.6	LPG dual fuel
Stock 1969 Rambler 343	3.0	31.5	3.1	
Percent Reduction	0	51	16	
Converted 1969 Ford 429	1.3	4.0	1.9	LPG
10 Converted 1970 Ford 250s	0.69	1.8	2.6	LPG
10 Stock 1970 Ford 250s	3.70	16.0	9.4	
Percent Reduction	81	89	72	
10 Converted 1970 Rebel 232s	0.51	3.9	3.1	LPG
10 Stock 1970 Rebel 232s	2.7	22.1	6.9	
Percent Reduction	81	82	55	

( )* indicates emission increase

indicated in Figure 6-2 (Ref. 6-6). This figure shows the California Seven-mode Cycle test results for a converted 1969, 327-CID Chevrolet engine operated at air-fuel settings ranging from 15 to 20.5; the sensitivity in CO emissions to the air-fuel ratio at settings up to 18 may be noted. Note also



* At conventional carburetor and ignition timing

Figure 6-2. Air-Fuel Ratio and Spark Timing Effects (Ref. 6-6) (1969, 327-CID Chevrolet, California Seven-Mode Test Cycle)

the improvement in NO_x emission control achievable at the extremely lean limits of operation made possible by the use of a gaseous fuel.

From a weighted average of the data presented in Table 6-2, it appears that exhaust emission levels of approximately 1.0 gm/mi HC, 4 gm/mi CO, and 3 gm/mi NO_x, as measured by the 1972 Federal Test Procedure, are achievable in conventional spark ignition engines equipped with existing propane fuel conversion hardware. Using relationships from Reference 6-7, these levels may be expressed in terms of the 1975 Federal Test Procedure and may then be compared with the original 1975 and 1976 Federal emission standards for light duty vehicles as shown in the following table:

	Emission Levels using Propane (gm/mi)	1975 Interim Standards (gm/mi)	Original 1975 Standards (gm/mi)	Original 1976 Standards (gm/mi)
HC	0.9	1.5	0.41	0.41
CO	2.9	15.0	3.40	3.40
NO_x	3.0	3.1	3.10	0.40

From these results, it appears that propane is capable of meeting the 1975 interim standards for all three pollutants and may also meet the original 1975 standards for CO and NO_x. With regard to the HC requirement for 1975, it is noted that, while propane HC emissions are approximately twice the standard, the photochemical reactivity of propane exhaust hydrocarbons is considerably lower than that for gasoline. The original 1976 requirement for NO_x does not appear to be attainable through the use of propane without additional engine control equipment. In this regard, it may be noted that a 1971 Olds Delta 88 equipped with LPG conversion kit, thermal reactor, and exhaust gas recirculation yielded the following improved emission results: 0.7 gm/mi HC, 2.2 gm/mi CO, 0.4 gm/mi NO_x (Ref. 6-8).

Nevertheless, because the emission control capability presently attainable through the use of propane fuel falls somewhat short of meeting the original 1976 federal baseline emission standards and, since vehicles tuned to achieve this capability show definite driveability problems, additional research is required.

6.2.4 Toxicity and Safety

Both propane and butane are relatively nontoxic gases and relatively safe. The Interstate Commerce Commission has stated that LP-gas is a safer fuel than either gasoline or diesel (Ref. 6-9). LP-gas does not puddle when spilled, and it quickly dissipates into the air (if the temperature is above the boiling point of the liquid). The flammability limits are very narrow, limiting the likelihood of accidental combustion. Since the equipment is designed as a pressurized container it is inherently sturdy and limits the possibility of rupture and fire should a vehicle be involved in an accident. In the event of a collision, an LP-gas tank has over 20 times the resistance of an ordinary gasoline or diesel tank.

6.2.5 Handling, Storage, and Distribution Requirements

Both propane and butane are generally stored and transported in a liquefied state by either pressurization in the storage container or by cooling below relatively moderate boiling points as a means of minimizing their volume for easier handling purposes. Of the two gases, propane is more generally suitable for on-the-road automotive vehicles because of its lower boiling point (advantageous in cold climates) and higher octane rating. Propane does, however, require higher tank storage pressures than butane to maintain it in a liquid state. For these reasons handling, storage, and distribution requirements for both two gases are somewhat complicated.

At present, neither propane nor butane is readily available to the motoring consumer as gasoline. Both can, however, be purchased from any of the more than 25,000 propane and butane dealers in the United States. These dealers are located in all large cities, along highways, and at most truck stops or recreational vehicle locations.

A vast amount of physical assets have been geared in the storage and transportation of propane and butane (for general purpose usage). At the end of 1971, these assets included more than 20,000 railroad tank cars, most of which exceeded 30,000 gallons in capacity; 28,500 transport and delivery vehicles; 72,000 miles of cross-country pipelines; a fleet of 150 barges and tankers;

9,200 bulk storage plants or distribution centers, and underground storage caverns having a total storage cpacity in excess of 7.2 billion gallons of LP-gas.

6.2.6 Critical Research Gaps

The emission control capability, presently attainable through the use of propane fuel, falls somewhat short of meeting the original 1976 federal standards. In addition, vehicles tuned so as to achieve this capability show definite driveability problems associated with lean operation. Reference 6-10, for example, reports that slugishness on response to acceleration and low power at high speeds were two problems encountered with lean-adjusted propane fueled vehicles. Performance deterioration at lean mixtures is also indicated in Figure 6-2. Thus, if propane were to be considered for use as an alternate fuel, further improvements in emission levels and vehicle performance at lean operating conditions would be desirable.

Propane availability and cost are additional factors which demand consideration in evaluating propane as an alternate fuel. A new raw material source and production process for obtaining LP-gas would be required to increase its availability. Therefore, an economically acceptable method of producing LP-gas directly from coal or oil shale is needed if it is to be considered as a viable alternative fuel.

6.3 CURRENT STATUS

6.3.1 Production Rates

LP-gas is produced at natural gas processing plants and at refineries, in the course of certain refining processes. The production of LP-gas (comprised mainly of propane and butane) has increased at an average annual rate of between 5 and 6 percent over the past 10 years. More than 200 oil and gas companies were domestically involved in producing in excess of 19 billion gallons of propane and butane in 1971 (Ref. 6-11). Table 6-3 presents the yearly production rates of LP-gas from 1961 to 1971. A further production breakdown in terms of the two basic LPG sources, the natural gas processing plants and the refineries, is given in Table 6-4. The major production source of propane and butane is seen to come from the natural gas processing plants, amounting to approximately 74 percent of the total LP-gas production.

Table 6-3. Annual Production of LP-Gas (Ref. 6-11)

(Thousands of Gallons)

Date	Propane	Butane	Butane-Propane Mixture	Iso-Butane	Other*	Total Production
1961	6, 344, 486	2, 658, 883	757, 718	806, 912	674, 012	11, 242, 011
1962	6, 333, 496	2, 636, 907	746, 011	845, 075	788, 656	11, 350, 145
1963	7, 252, 476	3, 002, 761	634, 182	971, 428	1, 145, 132	13, 005, 979
1964	7, 791, 469	3, 168, 093	554, 258	1, 014, 934	1, 300, 551	13, 829, 305
1965	8, 177, 271	3, 074, 379	595, 132	1, 113, 008	1, 351, 449	14, 311, 239
1966	9, 168, 793	3, 722, 368	997, 696	1, 188, 355	-	15, 077, 212
1967	10, 159, 783	4, 021, 651	1, 099, 581	1, 282, 630	-	16, 563, 645
1968	10, 867, 290	4, 238, 976	988, 344	1, 297, 590	-	17, 392, 200
1969	11, 427, 738	4, 661, 706	760, 284	1, 201, 536	-	18, 051, 264
1970	12, 011, 706	4, 597, 320	629, 034	1, 355, 508	-	18, 593, 568
1971	12, 834, 738	4, 544, 190	426, 342	1, 433, 334	-	19, 238, 604

* This category discontinued by the Bureau of Mines after 1965

Table 6-4. Source Production of LP-Gas (Ref. 6-11)

Type	Source, thousands of gallons		
	Production at Natural Gas Production Plants	Production at Refineries	Total Production
Propane	8,910,006	3,924,732	12,834,738
Butane	3,718,848	904,176	4,623,024
Butane-Propane Mixture	175,266	251,076	426,342
Iso-Butane	1,354,500	-	1,354,500
Total	14,158,620	5,079,984	19,238,604

Since proven natural-gas resources in the United States are rapidly being depleted, it would appear that the production of natural gas will peak out and then decline in the future, eventually eliminating this as an important source for LPG. In this event, it may be possible to augment the supply of LPG by modifying the refining operations in the United States so as to increase LPG production by additional cracking or other processing of the heavier distillate components of crude oil. Another possible future source of LPG is synthesis from coal by either the gasification or liquefaction route. At present, however, the synthesis process as applied to the production of propane would appear to be less efficient in terms of energy utilization than, for example, the production of gasoline.

6.3.2 Consumption and Uses

The consumption of LP-gas in 1971 between the various users is presented in Table 6-5 in order of diminishing use rates. The major consumption of LP-gas is seen to be in the areas of residential and commercial usage (39.9 percent of total consumed), chemical and synthetic rubber industries (26.6 percent of total consumed), gasoline production (17.4 percent of total consumed), and internal combustion engines (6.9 percent of total consumed). Typical uses of LP-gas are many and varied. In homes, LP-gas

Table 6-5. LP-Gas Consumption - 1971

LP-Gas Use	Percentage of Total Use
Residental and Commercial	39.9
Chemicaland Synthetic Rubber	26.6
Gasoline Production	17.4
Internal Combustion	6.9
Industrial and Refinery Fuel	4.7
Export	2.0
Miscellaneous and Secondary Recovery	1.4
Utility Gas	1.1
	100

is used for cooking, water heating, heating and air conditioning, clothes drying, etc. Around homes, LP-gas heats swimming pools, fuels barbecue grills, and provides outdoor light and heat. On the farm, LP-gas powers trucks and tractors, destroys weeds, dries crops, broods chicks and pigs, cures tobacco, runs irrigation pumping engines,and heats stock tank water. Commercially, LP-gas has a wide variety of uses as engine fuel for trucks, buses, lift trucks, taxi fleets, stationary engines, and as feed stock for the chemical, synthetic rubber,and gasoline industries.

6.3.3 Consumer Costs

The consumer costs of LP-gas has increased sharply in recent months, due to the high demand and limited domestic supplies currently available. The Oil Daily Price Listings for LP-gas group 3 (Tulsa, Oklahoma) shipments, for example, have increased by over 130 percent from September 5, 1972 to September 28, 1973. In this rapidly changing market, any listing of current prices may soon become obsolete. The prices of propane in bulk lots of 100,000 gallons or more, as of 30 November 1973 in the Los Angeles area, averaged between $0.39 to $0.47 per gallon depending on the bulk amount sold, and was generally similar to the price of gasoline at that time. On the basis of Btu per dollar, before the present price increase gasoline was running about 30 to 40 percent cheaper than propane.

6.4 PROJECTED STATUS

The future availability of LP-gas as an alternative fuel does not look encouraging for either the near term or the longer term. In the near term, the production of LP-gas is tied directly to the production rates at the natural gas processing plants and the gasoline refineries, or more simply to our domestic production of petroleum products. Though the production of LP-gas is expected to rise in the 1970s, the annual increase is expected to taper off from that experienced in the 1960s to an average annual increase of 4.7 percent (Ref. 6-12). The reason for the tapering off of LP-gas production increase is due in large part to the fact that the newer oil well finds are generally drier (i.e., less wet gas).

Because the current major production source of propane and butane is natural gas processing plants, a new raw material source and production process for obtaining liquid petroleum gas would be required to increase its availability. Therefore, economically acceptable methods of producing liquid petroleum gas directly from coal or oil shale are needed if it is to be considered as a viable alternative fuel. But even if costs of production of liquid petroleum gas from coal by either gasification or liquefaction are reduced, the production of gasoline from coal would be more efficient in terms of energy utilization. Considering this factor as well as the problems in establishing a nationwide distribution and storage system,this fuel is not considered a primary candiate for large-scale antomotive use. Rather, it may find application to commerical fleet operations.

SECTION 7

ETHANOL AND ETHANOL-GASOLINE BLENDS

7.1 CHARACTERIZATION

7.1.1 Fuel Type

Ethyl alcohol (also ethanol) is the hydroxyl derivative of ethane and has the chemical formula C_2H_5OH. It is mainly known by virtue of its use in alcoholic beverages as the principal product of fermentation.

At normal ambient conditions, ethanol is a clear, colorless, combustible liquid. It has a fairly broad liquidus range, freezing at $-114^{\circ}C$ and boiling at $+78^{\circ}C$, with a specific gravity of 0.79. Produced over the centuries by fermentation of various carbohydrates (sugars), which reached a zenith in this country during World War II, ethanol is now mainly manufactured synthetically from petroleum-derived ethylene for industrial use. The first commerical process for ethylene-based alcohol dates back to 1930.

The principal industrial uses of ethanol are as a chemical intermediate, as a solvent, as an antifreeze, and in fine chemical manufacture such as drugs, polishes, perfumes, cosmetics, etc. Alcohol has been used as a rocket and automotive fuel but has been replaced by more energetic fuels (e.g., kerosene, hydrogen) in the former instance and gasoline in the latter. Almost all industrial alcohol used in this country is sold in denatured form.

Alcohol content in commercial ethanol is expressed in terms of "proof" which in the U.S. is twice the concentration by volume. Thus a 190-proof alcohol contains 95% (volume) ethanol. Typical specifications for 190 for 190- and 200-proof alcohol are given in Table 7-1.

The specifications are designed to allow alcohol requirements to be met by either fermentation-produced or synthesis-produced ethanol.

Table 7-1. Typical Ethyl Alcohol Specifications

Requirement	190° Proof	200° Proof
Specific gravity, 60/60°F, max.	0.816	0.794
Purity, % by vol, min.	95	99.9
Acidity, % by wt as HOAc,* max.	0.002	0.002
Nonvolatile matter, g/100ml, max.	0.002	0.002
Miscibility with water	Complete	Complete
Permanganate time test, minutes, min.	50	30
Odor	No foreign or residual	--
Color, APHA,[a] max.	10	10
Water, % by wt, max.		0.1

[a] Refer to American Chemical Society Procedures, Specifications of Reagent Chemicals, 1960 ed., ACS, Washington, D.C., 1961

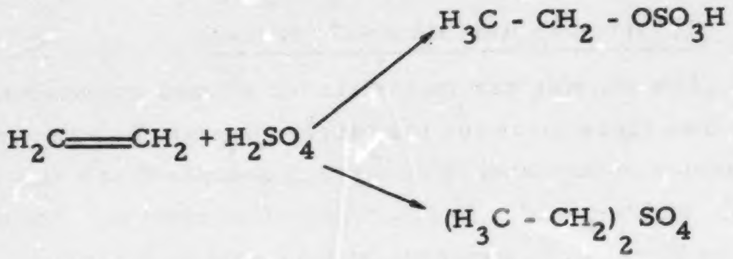
The major producers of ethyl alcohol also market the specially denatured and completely denatured alcohols, as well as various proprietary solvents in which ethyl alcohol is the basic ingredient. These various products can also be described by rigid and descriptive specifications, but the requirements must make allowances for the chemical and physical character of the denaturants.

7.1.2 Reserves or Raw Material Sources

The starting raw materials for ethanol manufacture are somewhat broader than those given for methanol. Most of the raw materials used in the manufacture of methanol (discussed in Section 4) can also be considered for ethanol, and the reader is referred to that section. The basic difference,insofar as direct U.S. commercial synthesis is concerned, relates to the use of petroleum-derived ethylene as feedstock from which ethanol is manufactured. Ethanol, however, is also being produced via Fischer-Tropsch synthesis and by fermentation of grain (thus the name grain alcohol is sometimes used), molasses, sulfite liquors, and other fermentable sugar- or starch-bearing agricultural products. Most of the ethyl alcohol production outside the United States is accomplished by the fermentation process and whenever demand has exceeded supplies in this country (World War II and Korean War), emergency production by fermentation increased. The raw materials came chiefly from molasses, fruits, and grains such as wheat and corn. Other raw materials include sawdust and sulfite liquors, potatoes, beets, and other agricultural products. Fermentation alcohol production is affected by very complex cost economics involving domestic availability and stability in the price of ethylene versus widely fluctuating availability of agricultural raw materials around the world. Historically, the price of fermentation enthanol in the U.S. has depended largely on competition for molasses which has tended to be a more stable commodity (except during the Cuban crisis) than grains. It should be noted that annual weather conditions exert a significant influence on availability of these crops. This makes the prediction such a difficult problem.

7.1.3 Methods of Manufacture

The two primary methods of ethanol synthesis involve the hydration of ethylene. The indirect hydration process involves reaction with concentrated sulfuric acid in an absorption column to form a solution of sulfates which are then hydrolyzed with water:



$$H_2C{=}CH_2 + H_2SO_4 \rightarrow H_3C - CH_2 - OSO_3H \quad ; \quad H_2C{=}CH_2 + H_2SO_4 \rightarrow (H_3C - CH_2)_2\,SO_4$$

$$H_3C - CH_2 - OSO_3H + H_2O \longrightarrow H_3C - CH_2 - OH + H_2SO_4$$

$$(H_3C - CH_2)_2\,SO_4 + 2H_2O \longrightarrow 2H_3C - CH_2 - OH + H_2SO_4$$

The alcohol and certain side products such as diethyl ether are separated from the spent sulfuric acid which is then reconstituted and recycled. A flow sheet for this process is shown in Figure 7-1.

The direct hydration process involves the catalytic addition of steam to ethylene at high pressure and temperatures

$$H_2C{=}CH_2 + H_2O \rightleftharpoons H_3C - CH_2 - OH$$

The catalyst commonly used is phosphoric acid on a suitable carrier, although other catalysts have been claimed to be effective. As in any catalytic process, yields depend upon proper control of reaction conditions as well as upon the catalyst used. With phosphoric acid catalyst the recommended conditions are about 300°C and 66 atm pressure with 66 percent (vol) water to ethylene in the feed stream. A flow sheet for this process is contained in Figure 7-2.

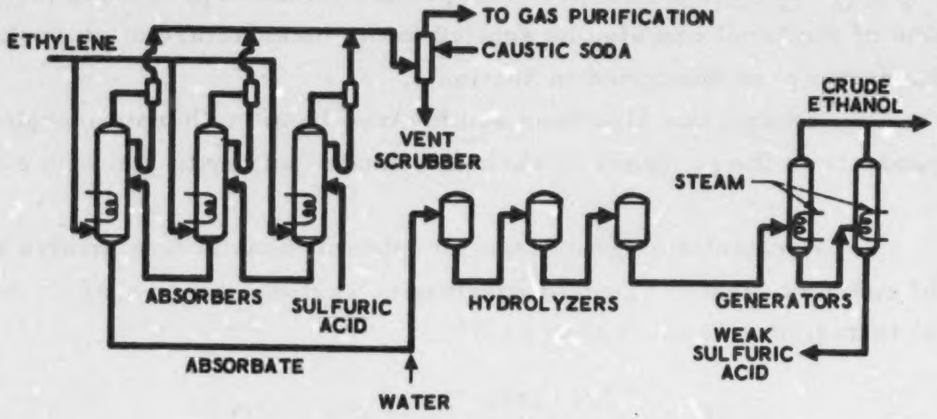

TO GAS PURIFICATION
ETHYLENE
CAUSTIC SODA
CRUDE ETHANOL
VENT SCRUBBER
STEAM
ABSORBERS
SULFURIC ACID
HYDROLYZERS
GENERATORS
WEAK SULFURIC ACID
ABSORBATE
WATER

Figure 7-1. Manufacture of Ethyl Alcohol by Esterification-Hydrolysis (Indirect Hydration)

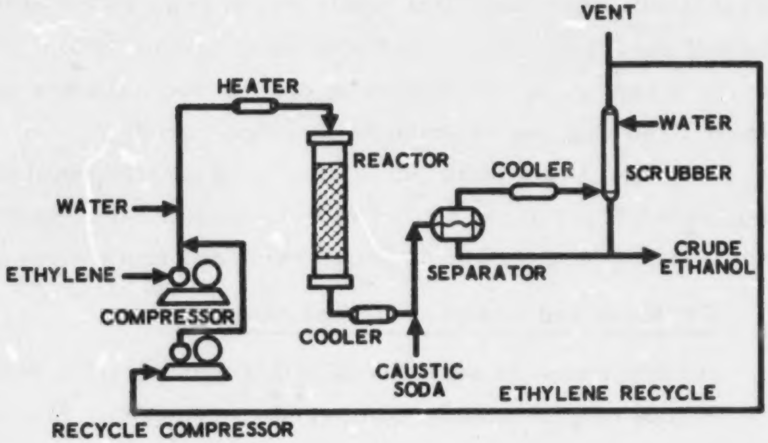

VENT
HEATER
WATER
REACTOR
COOLER
SCRUBBER
WATER
ETHYLENE
SEPARATOR
CRUDE ETHANOL
COMPRESSOR
COOLER
CAUSTIC SODA
ETHYLENE RECYCLE
RECYCLE COMPRESSOR

Figure 7-2. Manufacture of Ethyl Alcohol by Direct Hydration of Ethylene (Ref. 7-1)

The Fischer-Tropsch and partial oxidation processes for the production of methanol can also be applied to the manufacture of ethanol. These have also been described in Section 4.

Ethanol has also been synthesized from methanol through vapor phase catalysis in the presence of carbon monoxide and hydrogen with a cobalt catalyst.

Fermentation processes for ethanol manufacture involve a series of complex yeast-originated enzymatic reactions upon sugars. In chemical terms, this is often shown as:

$$C_6H_{12}O_6 \xrightarrow{\text{ENZYME}} 2C_2H_5OH + 2CO_2$$

The reactions may be thought of as very slow catalytic conversions, the enzymes acting as catalysts. The processes occur at near-ambient temperature and pressure in batch-reactor vessels called fermenters. Conversion times are measured on the order of 2 to 3 days, at which time the alcohol volume concentration is about 6 to 9 percent. As in other conversions previously described, side reactions occur which require careful process and culture (catalyst) controls. At the completion of fermentation, the product, called liquor or "beer," goes to a series of distillation columns where concentrated alcohol and various byproducts are recovered.

A typical yield from one gallon of blackstrap molasses is 1/2 gallon of 95-percent ethanol. A bushel of corn yields 2-1/2 gallons, and one ton of dry wood yields 55 gallons, although recovery from wood bark is lower.

7.1.4 Physical and Chemical Properties

As discussed in sections of this report dealing with methanol, properties of ethanol are frequently compared to gasoline. Since gasoline is a mixture of hydrocarbons, the properties given in Table 7-2 are compared to isooctane, which is a representative gasoline constitutent. The most important difference is seen to be in the heat of combustion, insofar as the use of ethanol as an engine fuel is concerned.

Table 7-2. Properties of Isooctane and Ethanol (Ref. 7-1)

Item	Isooctane	Methanol
Formula	C_8H_{18}	C_2H_5OH
Molecular weight	114.224	46.07
Carbon to hydrogen weight ratio	5.25	4.0
Carbon, % by weight	84.0	52.0
Hydrogen, % by weight	16.0	13.0
Oxygen, % by weight	0.0	35.0
Boiling point, F at 1 atm	210.63	173.0
Freezing point, F at 1 atm	-161.28	-173.4
Vapor pressure, psia at 100 F	1.708	2.5
Specific gravity, 60 F/60F and 1 atm	5.795	6.63
Coefficient of expansion 1/F at 60 F and 1 atm	0.00065	0.00048
Surface tension, dynes/cm at 68 F and 1 atm	18.77	23
Viscosity, centipoises at 68 F and 1 atm	0.503	1.17
Specific heat of liquid, Btu/lb-F at 77 F and 1 atm	0.5	0.6
Heat of vaporization, Btu/lb at boiling point and 1 atm	116.69	361
Heat of vaporization, Btu/lb at 77 F and 1 atm	132	395
Heat of combustion, Btu/lb at 77 F		
Higher heating value	20,556	12,780
Lower heating value Liquid fuel-gaseous H_2O	19,065	11,550
Stoichiometric mixture, lb air/lb	15.13	9.0
Autoignition temperature, °F	784	685
Octane no.	100	106

7.2 SUITABILITY FOR USE AS AN ENGINE FUEL

7.2.1 Engine/Vehicle Compatibility

Ethanol has been demonstrated to be compatible as a motor fuel with present vehicles. In many parts of the world it has been blended in concentrations varying between 10 and 20 percent to alleviate gasoline shortages. Like methanol, it has not proven to be economical for such usage in the United States because it has a lower calorific value per unit weight of volume than gasoline while being more costly than domestic gasoline.

7.2.2 Fuel Economy Effects

Studies over the years have demonstrated that the use of alcohol as an automotive fuel reduces fuel mileage essentially in proportion to the reduction in lower heating values of the vaporized fuels. For pure ethanol this corresponds approximately to a 60 percent increase in fuel consumption. Experiments in single cylinder engines and multicylinder engine-powered vehicles generally have tended to verify this. However, fuel consumption is influenced to some degree by the type of engine used and the duty cycle.

While much information appears in the literature concerning fuel economy effects of ethanol and ethanol/gasoline blends in spark ignition engines, they will not be cited in detail because publication was prior to World War II.

More recent work shows that the engine and the test conditions bear upon the comparative results, as published in a paper by Lawreson and Finigan (Ref. 7-2). Using a 1962 Oldsmobile V-8 (10.5:1 combustion ratio) and four different fuel blends (two alcohol-free gasolines and two containing 25 percent ethanol 190 to 200 proof), these investigators determined specific fuel consumption relative to motor load conditions. The fuels were as follows:

Blend 1: A commercially available 100 octane gasoline with a phosphorous additive

Blend 2: A 98 octane blend comprised of 92.5 octane unleaded gasoline and 3.0 ml of tel/gal

Blend 3: A 97.5 octane blend comprised of 75% (by vol) of 92.5 octane unleaded gasoline (as in Blend 2) and 25% of 200 proof ethanol

Blend 4: A 75% (vol) blend of 92.5 octane unleaded gasoline and 25% of 190 proof ethanol.

Figure 7-3 shows that at reduced engine loads the bsfc was greater with the 200-proof ethanol blend than with gasoline (leaded) but the differences were nullified at WOT (wide open throttle) conditions.

When translated into road economy figures versus speed, the authors stated that "the 190-proof alcohol blend was noticeably less efficient" while "the 200-proof blend produced essentially the same economy as the commercial gasoline except for a superiority at the higher road speeds for the latter". This is shown by Figure 7-4.

Kilayko (Ref. 7-3) reported results of comparison tests between gasoline (92 octane) and 190-proof ethanol in a 4-cylinder Renault engine. With gasoline as the fuel, engine compression ratio was 7.25:1 and with alcohol the compression ratio was increased to 12:1. With spark timing adjusted for maximum power, the tests showed that improved efficiency could be obtained by operating the higher-octane rated ethanol at the higher compression ratio. The following table shows that at the same engine speed and fuel-air equivalence ratio ($\phi^* = 0.9$) the specific fuel consumption was 0.76 (ethanol) vs 0.52(gasoline), which is less than a 50 percent increase in consumption.

Fuel	Compression Ratio	ϕ^*	Speed (rpm)	Bsfc (lb/hp-hr)	BMEP (psig)
Gasoline	7.25	0.9	2400	0.52	87
190° EtOH	12:1	0.9	2400	0.76	99

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[*] $\phi = \dfrac{\text{actual fuel-air ratio}}{\text{stichiometric fuel-air ratio}}$

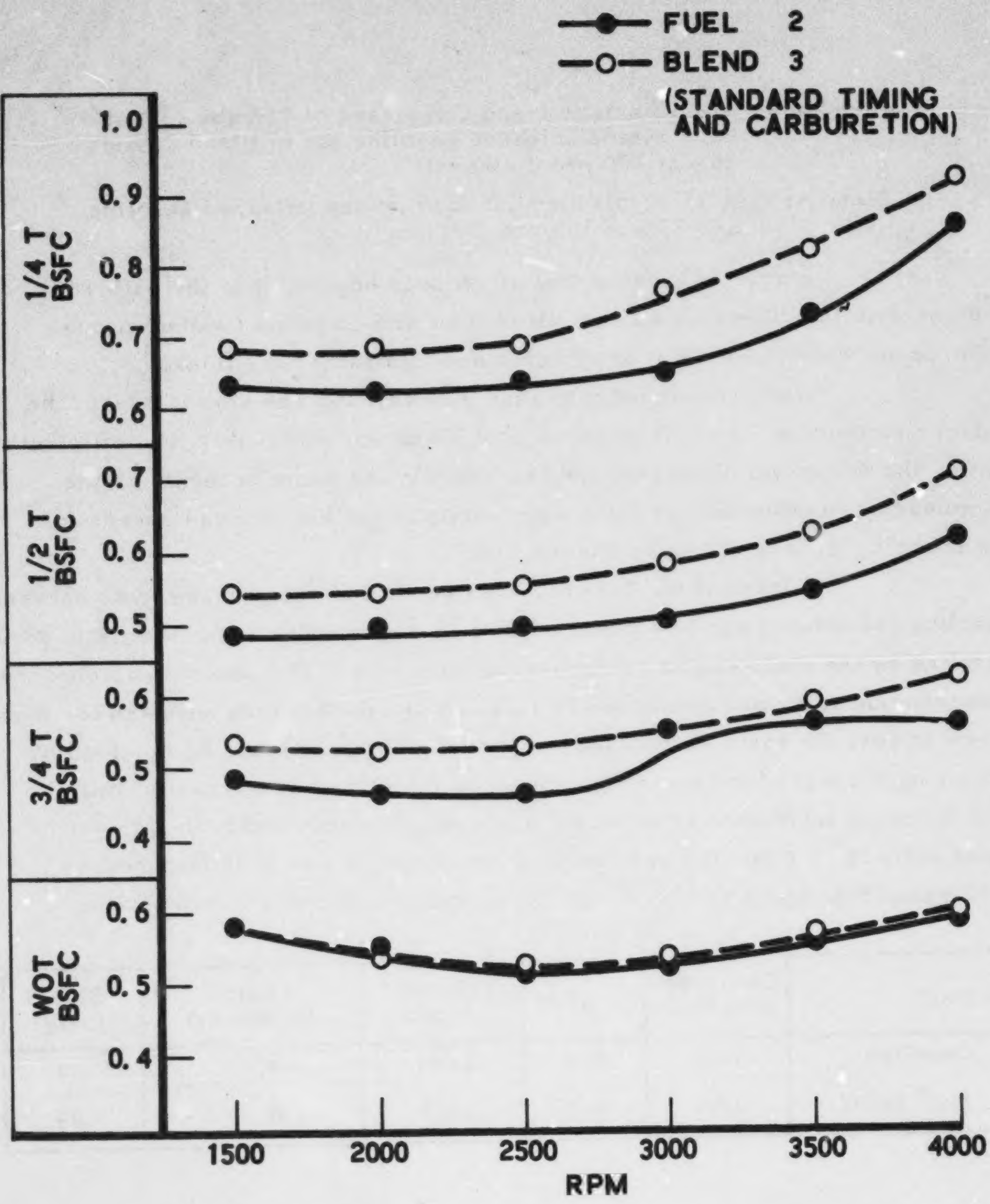

Figure 7-3. Efficiency at Loads - 1962 Oldsmobile (Ref. 7-2)

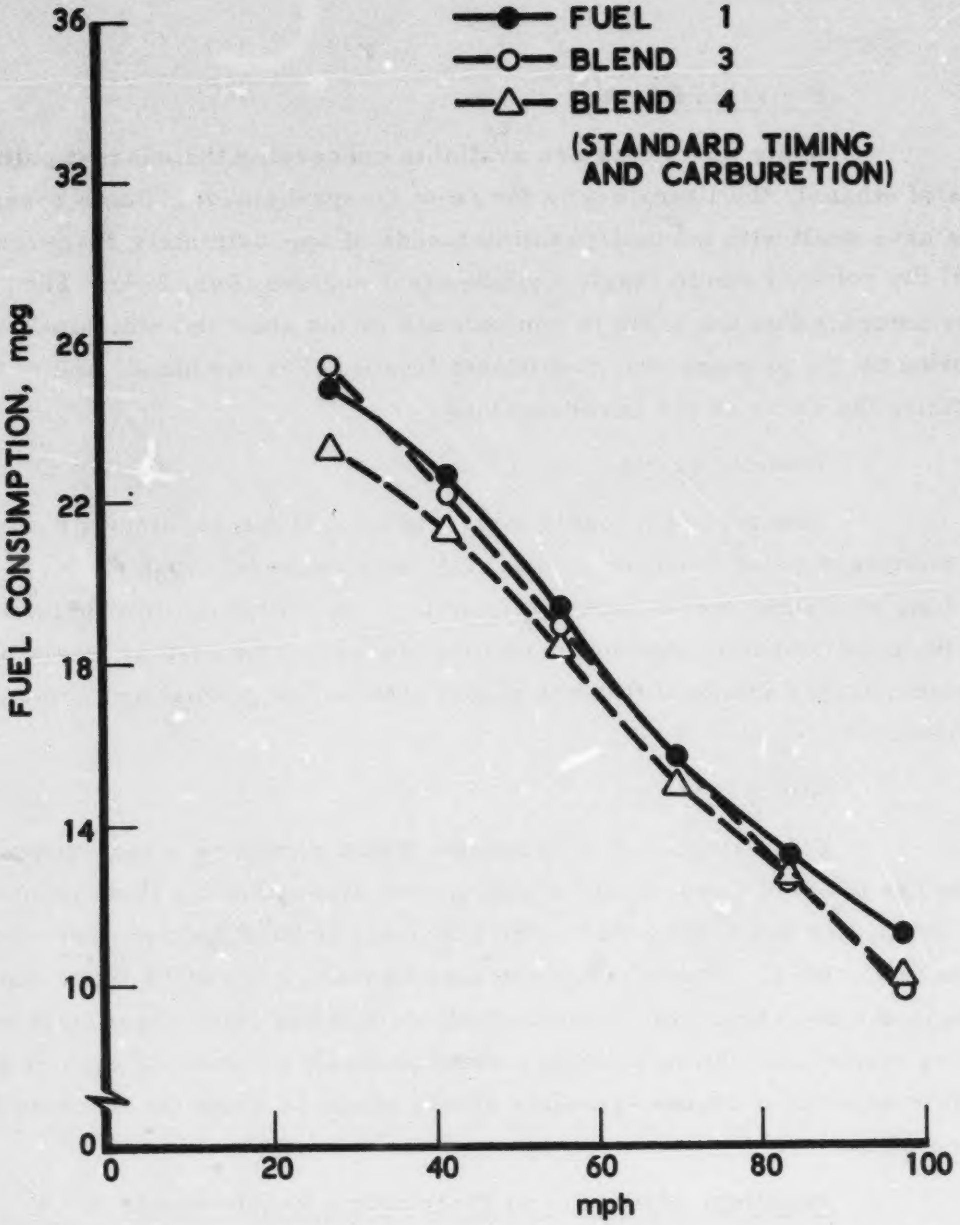

Figure 7-4. Road Load Economy - 1962 Oldsmobile (Ref. 7-2)

7.2.3 Emission Effects

While some data are available concerning the exhaust pollution effects of ethanol, the literature is far from comprehensive. Some recent efforts have dealt with ethanol/gasoline blends of approximately 25-percent ethanol (by volume) run in single-cylinder test engines (Ref. 7-4). The results compared on the basis of equivalence ratios show the emissions are controlled by the primary fuel constituent (gasoline) in the blend, and are essentially the same as for gasoline alone.

7.2.4 Toxicity Effects

Ethanol is not highly toxic. If inhaled for continuous periods under poor ventilation conditions, discomfitures occurs: coughing, eye irritation, headache, and related symptoms. The threshold limit value is 1,000 parts per million. Alcohol ingestion causes intoxication at levels below 100 grams; larger intake will cause stupor (150 to 200 grams) and poisoning (250 grams).

7.2.5 Safety Effects

Ethyl alcohol is a flammable liquid requiring a red explosive label by the ICC and Coast Guard shipping classifications; its flash point is 70°F, which lies below the established ICC limit of 80°F but far above that for gasoline, -40°F. Vapor concentrations between 3.3 and 19.0 percent by volume in air are explosive. Liquid ethyl alcohol can react vigorously with oxidizing materials. As this alcohol would probably be used, if used at all, the safety aspects of ethanol-gasoline blends would be about the same as for gasoline alone.

7.2.6 Handling, Storage, and Distribution Requirements

Commercial ethyl alcohol is shipped in railroad tank cars, tank trucks, five- and 55-gallon drums, and in smaller glass or metal containers having capacities of a pint, quart, U.S. or Imperial gallon. The 55-gallon drums may be of the unlined iron type. If a guarantee of more meticulous quality is desired, the drums may be lined with phenolic resin. The problem of contamination or adulteration by water is similar to that for methanol.

7.2.7 Ethanol-Gasoline Blends

Much of the preceding discussion has already dealt with ethanol-gasoline blends inasmuch as cost and reduced fuel economy, in the absence of other advantages, have militated against use of neat alcohol. Indeed, even the blends have little to recommend them. The most favorable test data indicate fuel economy about equal to that of gasoline. With regard to emissions, the general consensus of published reports is that ethanol-gasoline blends give the same carbon monoxide, hydrocarbon, and oxides of nitrogen levels in the exhaust as gasoline at the same equivalent air-fuel ratios (Ref. 7-5). The rationale of using ethanol as an antiknock replacement for tetraethyl lead is not convincing since there are other compounds (e.g., methyl alcohol) that are cheaper and at least as efficient.

The tendency of ethanol-gasoline blends to separate upon water addition is similar to, but not as strong as, that previously described for methanol. For example the water that can be tolerated by a 25 percent alcohol blend at room temperature is about one percent. For ethanol, however, this causes an additional problem. Water might be added purposely to obtain tax-free alcohol for drinking. The taste and odor of gasoline in the separated alcohol could be removed by shaking with activated carbon. Denaturing of the alcohol will be essential, whether used neat or in a gasoline blend.

Although ethanol-gasoline blends have a higher vapor pressure than the gasoline alone, the vapor pressure increase is much less than in the case of methanol-gasoline blends. Some removal of the butane from the gasoline would be required to achieve the same vapor lock protection for the ethanol-gasoline blend as for the neat gasoline.

In light of the current and projected high cost of ethanol and the lack of any significant advantage when added to gasoline, it does not appear these blends warrant serious consideration as a replacement for gasoline alone. If the alcohol-gasoline blends have any viability as future automotive fuels, the one selected for further evaluation should be methanol.

7.2.8 Critical Research Gaps

If ethanol is seriously considered for gasoline blends, more data are needed on miscibility and vapor lock problems using modern gasolines.

7.3 CURRENT STATUS

7.3.1 Production Rates

Recent production level figures for 1965 showed a total ethanol production (190° proof) of 175 million gallons, and of this amount over 80 percent (147 million gallons) was produced sythetically, with the rest comprised essentially of grain fermentation alcohol. In 1973, production was 245 million gallons of synthetic ethanol.

7.3.2 Uses

Domestic usage for years 1960 to 1964 are shown in Table 7-3. A significant proportion of ethanol production is used in acetaldehyde manufacture.

7.3.3 Consumer Costs

The price history of industrial ethanol in the United States is shown in Table 7-4. Unless a low-cost route to ethanol manufacture is found, ethanol cannot compete with other prospective fuels such as methanol.

7.4 PROJECTED STATUS

7.4.1 Availability

Although ethanol is being produced in large quantities, projected availability is not expected to improve in the near term to the level required to support its use as a motor fuel.

7.4.2 Projected Consumer Costs

Various projections are possible depending upon raw material costs, the type of process (synthesis versus fermentation), and related factors. The lowest-cost production route over the near term will continue to be synthesis from cracked hydrocarbons. The cost for fermentation process alcohol from grain has been estimated as about $1 per gallon or $12 per million Btu, except when sulfite waste liquor or waste wood is used as raw

Table 7-3. U.S. Consumption of Specially Denatured Alcohol, Fiscal Years 1960-1964[a] (Total disappearance, thousand wine gal, 190° proof alcohol) (Ref. 7-1)

Use	1960	1961	1962	1963	1964
acetaldehyde	156,348	148,948	138,334	145,113	104,072[b]
other chemicals	57,760	56,392	61,966	58,317	96,788[b]
solvents solvent and thinners for cellulose, shellac, resins, etc.	31,961	28,760	29,779	29,960	29,400
toilet preparations	11,621	12,718	16,859	21,977	26,766
processing, foods, drugs, other products	9,034	9.020	9,302	8,765	8,843
parmaceutical products for external use	4,107	3,860	4,614	4,518	4,377
detergents, flavors, disinfectants, and other solutions	10,602	12,174	12,641	11,430	12,160
Total	67,325	66,532	73,195	76,659	81,546
fluid[c]	173	187	184	158	127
fuel	528	434	506	453	477
laboratory and experimental use	1,026	1,204	1,616	1,437	1,812
Grand Total	283,160	273,696	275,801	282,137	284,822

[a] Figures published by the U.S. Business and Defense Services Administration.

[b] Changed pattern may be due to change in usage classification.

[c] Antifreezes, brake fluids, cutting oils, etc.

Table 7-4. Price History of Industrial Ethyl Alcohol in the United States (Ref. 7-1)

Year	Price,[a] ¢/gal, tank quantities	
	190° Proof	S.D.-1[b]
1950	39.0	41.0
1951	89.0	57.5
1952	55.0	57.0
1953	48.0	50.5
1954	40.0	42.5
1955	40.0	42.5
1956	42.0	44.5
1957	47.0	49.5
1958	47.0	49.5
1959	52.0	54.5
1960	52.0	54.5
1961	52.0	54.5
1962	52.0	54.5
1963	52.0	54.5
1964	52.0	54.5

[a] Between 1948 and 1955 a 5 cents per gallon differential existed between 190 and 200 proof; since 1955, the differential has been 7 cents.

[b] Typical of denatured formulations.

material. The cost then drops to about $6 per million Btu (Ref. 3-7), with an additional $1.10 per million Btu for distribution to the consumer.

7.4.3 Capital Costs and Timing Implications

The capital costs for ethanol synthesis plants appear to be slightly above those for methanol production. A recently installed USI Chemicals Company operation with an annual capacity of 60 million gallons per year reportedly cost $16 million. Based on a 350-day operation, this amounts to a daily capacity of 171,000 gallons per day or $93 per daily gallon capacity. Fermentation plants tend to differ from each other. Plants using molasses require lower capital investment than grain because of the absence of grain handling and by-product feed recovery operations. Capital costs for large-scale fermentation plants must still be determined. For competitive processes, a figure of $0.10 per gallon would require an investment of less than $275 per daily gallon at a return of 12-1/2 percent. For 100,000 barrels per day production this represents over $1 billion investment.

7.4.4 Impact With Other U.S. Energy Requirements

Unless ethanol can be economically produced from waste products or very low cost raw materials its use as motor fuel will be very limited. Ethanol produced as a by-product in Fischer-Tropsch synthesis will also have minor impact.

7.4.5 Factors Which May Inhibit Use

Economics of ethanol production and poor fuel economy are the major factors tending to limit its use. It is also susceptible to water contamination and adulteration.

7.4.6 Critical Technology Gaps

New methods are needed to enable low-cost synthesis of ethanol on a very large production scale.

SECTION 8

HYDROGEN

This section discusses pure hydrogen as a potential alternative fuel. Hydrogen gaseous blends or hydrogen/gasoline fuel mixtures are discussed in Section 11, "Fuels Reformed On-Board the Vehicle."

8.1 CHARACTERISTICS

Hydrogen, H, is the first element in the periodic table. Its principal source is water. Hydrogen was first recognized in about the 15th century. It was discovered that water was formed when hydrogen burned in air. The name "hydrogen" is derived from a similar Greek word meaning water producer.

8.1.1 Fuel Type

Hydrogen appears to be suitable for use as an automotive fuel. Hydrogen is stable and relatively unreactive at ordinary temperature. It reacts with oxygen to form water: $2H_2 + O_2 \rightarrow 2H_2O$. This reaction is exothermic, producing 51,600 Btu per pound of hydrogen (lower heating value). At temperatures of about 500°C or higher, this reaction proceeds spontaneously. At lower temperatures, the reaction occurs in the presence of a suitable catalyst, such as platinum or palladium, or if activated by a spark.

Hydrogen has been used successfully as a fuel on internal combustion engines with fuel mixtures of hydrogen-oxygen, hydrogen-air, and hydrogen-air-gasoline. Early problems of engine knock, preignition, and backfire have largely been resolved (Ref. 8-1).

The United States space program created a large demand for hydrogen, both as a primary rocket engine fuel for combustion—principally with oxygen, and as a propellant for conceptual nuclear-powered space vehicles. But its main use in this country is in the production of ammonia.

8.1.2 Reserves or Raw Material Sources

Hydrogen can be produced from all fossil hydrocarbons including natural gas, oil refinery gas, LPG (propane and butane), natural gasoline, naphtha, fuel oil, crude oil, coal, and coke. Hydrogen can be also produced from water by separating the chemical bond between hydrogen and oxygen by the addition of energy. The supply of hydrogen from water is virtually inexhaustible, although facilities for mass production are not yet available.

Estimates of known and yet to be discovered resources of hydrocarbons in the United States are shown in Table 8-1. By 1985, the annual domestic energy supply from all sources is estimated to be 131.5 $\times 10^{15}$ Btu. Of this 96.9×10^{15} Btu will be derived from fossil hydrocarbon sources. The total annual energy demand at that time will be 130.0×10^{15} Btu. Of this 29.0×10^{15} Btu or approximately 22 percent will be required by the transportation sector (Ref. 2-1).

8.1.3 Methods of Manufacture

Hydrogen is currently produced primarily from hydrocarbons, using steam reforming or partial oxidation processes. Its main use is in the production of ammonia. Hydrogen is also commercially produced from water electrolysis. Water electrolysis is accomplished by passing a direct current

Table 8-1. Domestic Resources of Fossil Hydrocarbons (Ref. 2-1)

Source	Resource Base
Natural Gas	1412.0×10^{12} CF ($1,457 \times 10^{15}$ Btu)
Crude Oil	472.3×10^{9} bbl ($2,739 \times 10^{15}$ Btu)
Oil Shale	1781.0×10^{9} bbl ($9,549 \times 10^{15}$ Btu)
Coal	3.2×10^{12} tons ($80,200 \times 10^{15}$ Btu)

between two electrodes immersed in an electrolyte (usually potassium hydroxide solution). Hydrogen is formed at the cathode and oxygen is formed at the anode. The rate of hydrogen production is directly proportional to the current passing between the electrodes. Thermal, thermochemical, and radiolytic processes are also potential, but as yet undeveloped, production methods. The world production of hydrogen from water is only 3 percent of the total hydrogen used in the U.S. (Ref. 8-2). This low percentage is due to the present low cost of hydrogen produced from hydrocarbons as compared with that produced from water.

Processes available for the production of hydrogen include the following:

a. Catalytic Steam-Hydrocarbon Reforming

Gaseous hydrocarbons, such as methane and ethane, and those which may be vaporized at moderate temperatures, such as propane, butane, and petroleum naphtha, are reacted with steam over a nickel catalyst at 1200° to 1800°F to produce carbon monoxide and hydrogen. This can be followed by a shift reaction in which the CO is converted to CO_2 and additional hydrogen produced by the action of water.

b. Pressure Noncatalytic Partial Oxidation of Hydrocarbons

Hydrogen and hydrogen-rich synthesis gases are produced from partial oxidation by burning hydrocarbons with oxygen or oxygen-rich gases. The advantage of this process over steam reforming is that it operates with any hydrocarbon feedstock that can be compressed or pumped, from natural gas to crude oil or asphalts.

c. Pressure Catalytic Partial Oxidation of Hydrocarbons

Hydrogen is produced from hydrocarbons in an autothermal self-sustaining process. The exothermic reaction of oxygen with the hydrocarbon and the endothermic reaction between hydrocarbons and steam and carbon dioxide maintains the required reaction temperature over a nickel catalyst bed. The hydrocarbons are converted to hydrogen and carbon dioxide.

d. Thermal Decomposition of Hydrocarbons

The endothermic thermal decomposition reaction $CH_4 \rightarrow C + 2H_2$ is carried out at 1200 to 1800°F and 10 to 30 psig pressure in a fluidized-bed reactor containing silica-aluminum-nickel catalyst particles on which carbon collects. The catalyst particles are withdrawn from the reactor and flowed to a regenerator through which air is blown to burn off the carbon and reheat the catalyst. The hot regenerated catalyst is carried back to the reactor with the feed gas stream.

e. Hydrogen from Coal

Coal is gasified by treating with oxygen at 450 psig and at combustion temperatures of approximately 2250°F. Most processes synthesize gas from coal in lump form, although gasification processes for powdered coal are available. The specific process used depends upon the availability of lump or powdered coal. The higher the calorific values in the process, the greater is the hydrogen yield. For this reason, a mixture of oxygen and steam is used in the process.

f. Electrolysis

Hydrogen has been produced commercially by water electrolysis for many years. Water electrolysis is accomplished by passing a direct current between two electrodes immersed in an electrolyte, usually a potassium hydroxide solution. Hydrogen is formed at the cathode, and oxygen is formed at the anode. For every two parts by volume of hydrogen formed, one part of oxygen is recovered. The process requires from 140 to 160 kW-hr of electric power per 1000 SCF of hydrogen produced. It is economical only where the cost of electricity is low (e.g., 6 mills/kW-hr) and where profitable use can be made of the oxygen.

g. Thermochemical

Thermochemical production of hydrogen is in an early experimental phase and involves the decomposition of water by the absorption of thermal energy in a multistage reaction series requiring high temperature in excess of about 600 to 700°C. Utilization of large amounts of thermal energy from a nuclear reactor or other primary heat source is necessary.

h. Radiolytic

Radiolytic production of hydrogen, also in the experimental phase, involves the direct absorption of nuclear energy by the water to form hydrogen and oxygen, which must then be separated. Considerable research in this area is required for a complete evaluation of merits. Meaningful cost estimates for this process are not available. As of now, it does not appear to be economically competitive with water electrolysis.

8.1.4 Physical and Chemical Properties

Liquid hydrogen is a transparent, water white, odorless liquid. When in an observable condition, it is usually boiling vigorously because of its low boiling point. When liquid hydrogen vaporizes in air, the gas can create an ignitable or, if confined, an explosive mixture. It will react violently with strong oxidizers igniting easily with oxygen and spontaneously with fluorine and chlorine trifluoride. All known substances are essentially insoluble in liquid hydrogen. Helium is probably soluable to the extent of 1 percent.

The hydrogen molecule H_2 contains two atoms, each consisting of a single proton in the nucleus and a single electron outside the nucleus. It is the lightest of all known substances, with an atomic number of 1 and an atomic weight of 1.0080. The physical and chemical properties of hydrogen are given in Table 8-2.

The diatomic hydrogen molecule exists in two forms, ortho and para. Each of the two atoms consists of a proton and an electron. Both parallel spin (same direction) and antiparallel spin (opposite direction) of the protons can occur in the molecules. Those molecules having parallel spins are termed orthohydrogen, while those having antiparallel spins are called parahydrogen. There is no difference in the chemical properties of the two forms, but there is a slight difference in the physical properties due to the difference in nuclear spins. The two modifications are usually found to be in equilibrium with one another. The equilibrium ratio of their concentrations is a continuous function of temperature. Freshly liquefied hydrogen which has not been catalyzed into a stable "para" state is not at equilibrium. On standing, this mixture, which is referred to as normal hydrogen, undergoes a slow shift towards the equilibrium concentration and in this process it loses about 20 percent of its volume during the first day due to boiloff. To prevent such evaporation losses, the normal hydrogen is converted rapidly to the stable parahydrogen by the use of a catalyst and energy extraction.

Table 8-2. Properties of Hydrogen (Ref. 8-3)

Chemical Formula	H_2
Molecular Weight	2.016
Density	
Vapor - gas at 2000 psi 0.667	0.005327 lb/ft^3
Liquid - at normal boiling point	4.43 lb/ft^3
Heating Value	
Volumetric Gross	270,274 Btu/ft^3
Weight Gross	228,693 Btu/ft^3
Weight Net	51,623 Btu/lb
Air for Combustion	
O_2 Weight	7.937 lb/lb
N_2 Weight	26.406 lb/lb
Air Weight	34.344 lb/lb
Products of Combustion	
CO_2 Weight	---
H_2O Weight	8.937 lb/lb
N_2 Weight	26.407 lb/lb
Flammable Limits	4.00-74.2%
Flame Velocity	9.2 ft/sec.
Ignition Temperature	1065°F
Theoretical Combustion Temperature	3887°F
Normal Transportation	
Normally carried as compressed gas in high pressure container. Can be shipped by pipeline. Could also be transported as a cryogenic liquid.	

8.1.5 Oxidizer Requirements and Combustion Characteristics

An unconfined mixture of hydrogen and air will burn but not detonate if it is exposed to a limited ignition source such as a spark. In confined areas or when ignition is accomplished by a shock source, equivalent to a blasting cap or a small explosive charge, an explosion can occur. Hydrogen burns readily and evenly in air with a very hot, nonluminous, and almost invisible flame. Flame temperature of hydrogen-air in stoichiometric proportions is about $2300^{\circ}K$. The burning velocity is dependent on the hydrogen-air mixture and reaches a maximum at about 40 to 45 percent hydrogen by volume. When no impurities are present, hydrogen burns in air with an invisible flame. Hydrogen-air mixtures containing as little as 4 percent and as much as 74 percent hydrogen by volume are readily ignited. Hydrogen-oxygen mixtures are flammable over the range of 4 to 94 percent hydrogen by volume.

8.2 SUITABILITY FOR USE AS AN ENGINE FUEL

8.2.1 Engine/Vehicle Compatibility

Hydrogen, with air from the atmosphere or with oxygen supplied on-board, offers an impressive potential for fueling future transportation systems. Hydrogen, the most energetic of chemical fuels, offers these critically important advantages: (1) it is available from water resources through the addition of energy from fossil, nuclear, or perhaps solar sources, and (2) it can be consumed with minimal environmental degradation. The use of hydrogen as a fuel for internal combustion engines, especially gas turbines and reciprocating types, has been proven technically feasible (Ref. 8-4). An historical review of application of hydrogen to internal combustion engines, together with some results of recent experimental work, is presented in References 8-5 and 8-6. Successful operation with lean air hydrogen mixtures and compression ratios up to 16:1 was demonstrated. Experimental work has demonstrated satisfactory engine operations with lean fuel-air ratios from 30 to 65 percent of stoichiometric. Operation at a fuel-air ratio of 45 percent of stoichiometric seems optimal, where the thermal efficiency was maximum and NO_x emissions were minimum.

In addition to conventional engine types, unconventional power plant designs such as stratified charge, diesel, rotary, and gas turbine engines appear capable of sustaining efficient combustion with hydrogen. This type of system offers the potential of extremely high thermal efficiencies and produces only water as exhaust, along with nitrogen and variable amounts of oxides of nitrogen.

One of the key problems with hydrogen which must be addressed is the mode of on-board storage. Hydrogen in its densest form (as a cryogenic liquid) is ten times the volume of the same weight of gasoline. Fortunately, it has approximately 2-1/2 times the heating value per unit weight as partial compensation. On an equivalent Btu basis, hydrogen requires 3-1/2 times the volume of gasoline. Four methods of storage on-board a transportation vehicle can be considered:

a. As a cryogenic liquid at $-423^{\circ}F$
b. As a pressurized gas at ambient temperature
c. As a metal hydride
d. In a chemical compound such as ammonia.

The cryogenic form appears to be best for automotive application based on existing technology. The pressurized gas form appears to require heavy, bulky, and hazardous containers for most applications. Research work is under way in hydride and chemical compound storage of hydrogen, but it is too early to assess ultimate feasibility.

A general conclusion is that hydrogen storage by any of these methods will take up considerably more volume than conventional hydrocarbon fuels and that substantial cost may be incurred in converting hydrogen gas to the stored form. Also the container will tend to be rather heavy, sophisticated in design, and probably very expensive. In addition, the filling and emptying of the storage unit will no longer be a simple operation. This appears to be an inherent problem with hydrogen vehicles. The bulky storage requirements will have a substantial impact on automotive layout and design.

Ground transportation vehicles may utilize conventional internal combustion engines converted to hydrogen fuel or unconventional hydrogen or hydrogen/oxygen power plants. In conventional engines some improvement in thermal efficiency may result from the shift to hydrogen due principally to its propensity for very lean operation at part-load conditions. However, major gains can be obtained from the development of basic cycle improvements and/or new operating cycles which can capitalize on hydrogen's outstanding heating value, combustion characteristics, and excellent cooling performance.

8.2.2 Fuel Economy

Experimental work using modified gasoline engines but fueled with hydrogen-air mixtures have shown good fuel economy.

A four-cylinder Toyota engine was modified to incorporate a special hydrogen induction technique (HIT) of varying the fuel-air ratio by varying the fuel charge and not by air throttling (Ref. 8-7). Thus, the part-load pumping losses encountered in a spark ignition engine are eliminated, resulting in high efficiency at light loads characteristic of urban driving. The part-load efficiency of the HIT engine was found to be higher than that of the throttled gasoline engine.

Fuel economy tests were performed on a four cylinder Pontiac engine (Ref. 8-7), converted to operate on hydrogen using the HIT technique. The specific fuel consumption (pounds of hydrogen per horsepower hour) is plotted as a function of spark advance at an average speed of 1,375 rpm and an average torque of 24 foot-pounds. It is observed in Figure 8-1, that for this combination of rpm and torque, the best economy setting is 50 plus or minus 2 degrees before top dead center. The gain in efficiency over that of a throttled gasoline engine at part load was realized. This is illustrated in Figure 8-2 where the ratio of Btu fuel consumed per horsepower hour for the

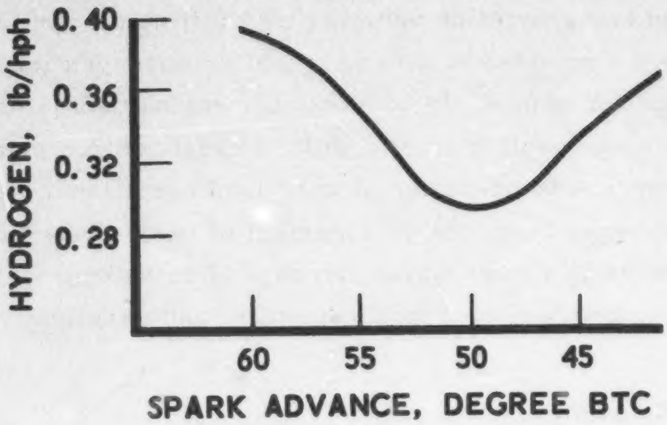

Figure 8-1. Specific Fuel Consumption (Ref. 8-7)

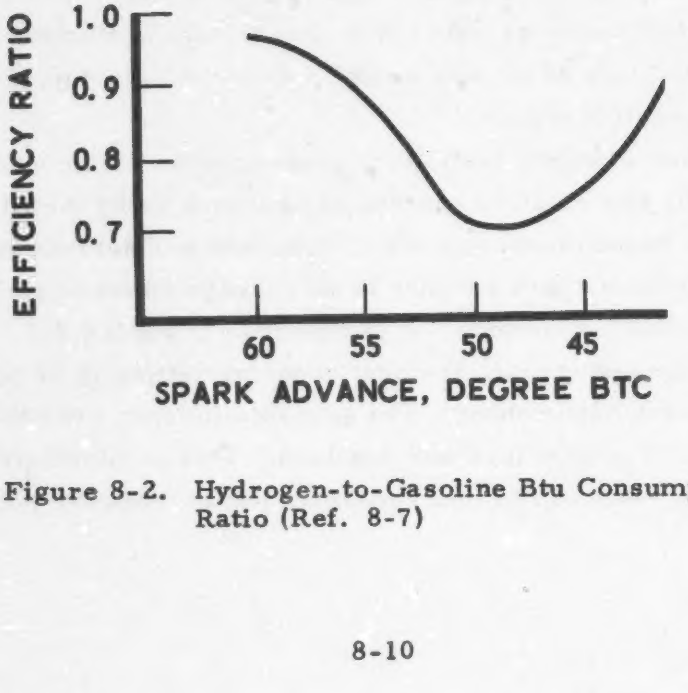

Figure 8-2. Hydrogen-to-Gasoline Btu Consumption Ratio (Ref. 8-7)

hydrogen engine to that of an essentially equivalent gasoline engine operating at the same part-load condition is plotted as a function of spark angle. It is observed that at the best economy spark setting (curve minimum value), the hydrogen engine reduces Btu input by about 30 percent. At light loads the percentage increase is even greater.

Using a Ford V-8 engine modified to recirculate a fraction of the exhaust gas (EGR), a UCLA hydrogen-fueled test car obtained 10 miles per pound of hydrogen under actual driving conditions, which corresponds to 5100 Btu per mile (Ref. 8-8), as compared to a similar gasoline-fueled car using, typically, 9000 Btu per mile.

Another project utilizing hydrogen generated by reforming gasoline on-board the vehicle is being carried out at Jet Propulsion Laboratory (Ref. 8-5). More details on this process are given in Section 11.

It has to be realized, however, that engine operation at lean mixtures and low reduced manifold-charge density because of low density of hydrogen, will result in maximum power loss of gasoline to hydrogen converted engines which may be of the order of 15 to 20 percent.

8.2.3 Emission Effects

Hydrogen itself appears to be an ideal fuel for the automobile engine for achieving low exhaust emissions. It is the cleanest possible fuel in use, with the complete absence of carbon. A number of approaches have been made toward operating conventional gasoline engines on hydrogen. Success has been attained in carrying out the necessary mechanical conversions, with indications that extremely low pollution levels have been achieved.

Under combustion with oxygen, hydrogen offers the complete elimination of hydrocarbons, carbon monoxide, and oxides of nitrogen. However, oxygen would have to be stored on-board the vehicle. With air combustion, emission of oxides of nitrogen are expected; the level of emission is dependent on the combustion temperature because NO_x emissions increase with increases in temperature. Low combustion temperatures are achievable by using lean fuel mixtures. Impressive results were achieved in the UCLA entry in the 1972 Urban Vehicle Design Competition (Ref. 8-1). This car, using a Ford V-8 engine with a propane carburetor operating on pure hydrogen fuel was tested by the California Air Resources Board and by the Environmental Protection Agency. The results in Table 8-3 show surprisingly low NO_x emissions, considering that none of the conventional antipollution equipment had been installed. The HC and CO emission results are most probably due to excessive lubricating oil combustion. The high CO_2 level tends to support the latter conclusion.

8.2.4 Toxicity Effects

Gaseous hydrogen acts as a simple asphyxiant. The physiological effect results from a decrease in available oxygen due to the presence of hydrogen. There are no natural warning properties, so an odorant has been considered. The precautions taken to prevent fire and explosion are more than adequate to protect against oxygen deprivation and consequence asphyxia.

8.2.5 Safety Effects

Hydrogen, being readily flammable in air, creates combustible mixtures with air. Because its flammability limits when mixed with air are very wide and its ignition energy is very small, a hydrogen fire is easier to create than a gasoline fire. The required safety precautions for handling hydrogen are therefore more stringent than those required for conventional fuels. The safety aspects of both gaseous and liquid hydrogen will be examined.

8.2.5.1 Gaseous Hydrogen

The occurrence of leaky hydrogen systems can pose a hazard. In contained spaces, however, the amount of energy released in a fire or explosion is low enough such that relatively small hydrogen explosions can be contained within the walls of laboratory glassware. In unconfined spaces, limited release of hydrogen tends to move away from the point of release since the density of hydrogen is only about seven percent that of air. On the

Table 8-3. Emissions from Hydrogen-Fueled Automobile, gm/mile (Ref. 8-1)

Test No.	HC	CO	NO_x	CO_2
1	0.20	0.44	0.850	9.72
2	0	0.32	0.205	Not Reported
1975 Federal Interim Stds	1.50	15.00	3.1	Not Stipulated
1977 Federal Stds	0.41	3.40	0.400	Not Stipulated

other hand, gasoline vapor tends to collect around a spill or leak, since its density is greater than that of air. This aspect is important when considering public reaction to the safety aspects of hydrogen. Although extremely rapid combustion of hydrogen can occur, the detonation of hydrogen-air mixtures is unlikely in unconfined spaces.

Extra precaution should be taken for leaks. Since the hydrogen flame is almost invisible, small hydrogen fires may go unnoticed. Severe burns to personnel may be caused by hydrogen flames from leaky equipment.

8.2.5.2 Liquid Hydrogen

Liquid hydrogen is hazardous because of its extremely low temperature. Burns and freezing of the skin and tissue will result if contacted by liquid hydrogen, cold hydrogen vapors, or cold pipes and valves.

Since liquid hydrogen has a very low viscosity, leakage through a ruptured tank occurs at a high rate. The chances of leakage are, however, remote, since hydrogen must be stored in double-walled, vacuum-insulated tanks.

The storage temperature of liquid hydrogen is below -423°F. This creates a significant and unique hazard. This temperature is low enough to liquefy all other gases except helium. Any part of the hydrogen tank or transfer line that becomes cooled to this temperature or close to this temperature and is exposed to air will liquefy the air. Because of the difference in boiling points between oxygen and nitrogen, the resulting liquid will become enriched in oxygen. Thus, an improperly insulated liquid hydrogen line can cause oxygen buildup, with a consequent dangerous fire hazard. For this reason, flammable materials cannot be used as insulation. In addition, foam insulation cannot be used unless the voids in the insulation are purged by either hydrogen or helium, the only gases that will not condense. Any air leaks in the insulation will present a fire hazard due to the presence of oxygen concentration by liquefaction. During transfer operations, hydrogen gas evolves. This gas must either be contained or be vented without being ignited.

8.2.6 Handling, Storage and Distribution Requirements

Some major drawbacks are found in the problems of distribution to service centers and in storage on-board the vehicle. To provide a vehicle with reasonable driving range, an energy content of about 20 gallons of gasoline, or about 2 million Btu, must be provided. A standard 2-cubic foot cylinder of compressed hydrogen at 2000 psi weighs about 125 pounds and contains only 1 pound of hydrogen, which is about 51,600 Btu. Thus, about 40 such cylinders would be required. Clearly, compressed gas is out of the question, even with lightweight cylinders. In liquid form, hydrogen has an energy density of 30,800 Btu/gal, so that a tank capacity of 110 gallons is required, over four times the size required for gasoline. A vacuum-insulated storage tank weighing about 300 pounds will be required, the fuel will add 43 pounds for a total weight of 343 pounds. For the same energy content, 20 gallons of gasoline will weigh about 119 pounds while the tank will weigh about 26 pounds for a total of 145 pounds.

Because liquid hydrogen must be maintained in vacuum-insulated tanks at below its boiling point of -423°F, the method of insulation and fabrication are complex and could prove too expensive. Such tanks are in routine laboratory use today, and large-scale transportation of liquid hydrogen is carried out by rail-tank car and by road tanker. The safety problems of liquid hydrogen tanks in these applications have been identified and reduced to acceptable risks.

A possibility exists for the use of a metal hydride that can be decomposed on the vehicle to provide hydrogen and that can be replenished at filling stations supplying hydrogen gas. The hydrogen is held inside the metal hydride by chemical bonds which are broken by heat addition. The use of a magnesium-nickel alloy hydride system has been suggested, but its weight and volume are still excessive (some 530 pounds plus a container) for matching the equivalent of about 20 gallons of gasoline. Another problem with this concept is the dissipation of the large amount of heat released when the fuel tank is filled and the hydride is formed.

Structural materials used for the storage and transfer of liquid hydrogen are of interest to the design engineer. For the low-temperature application, materials should be selected on the basis of their structural properties such as yield strength, ductility, impact strength, and notch sensitivity. The material must also be metallurgically stable, so that phase changes in the crystalline structure will not occur under repeated thermal cycling. Hydrogen-created blistering and embrittlement of metal may be avoided by the use of protective coatings and of the proper alloys. Low-alloy carbon steel becomes brittle at liquid hydrogen temperatures and should not be used. Ferritic and martensite stainless steels have poor ductility at low temperature and are not recommended for cryogenic use. As a rule, copper, brass, aluminum, monel, nickel, and authentic or 300 series stainless steels are satisfactory.

8.2.7 Critical Research Gaps

The technical suitability of hydrogen as an automotive fuel has been demonstrated by the limited experiments to date. Before hydrogen can be seriously considered for widespread use as an automotive fuel, considerable research efforts are required. These include:

a. Automobile storage method for hydrogen whether gaseous, liquid, hydride, or chemical compounds

b. Combustion and mechanical efficiency characteristics of alternative engines operating with hydrogen fuel

c. Performance of hydrogen-engine-powered automobiles as measured by exhaust emissions, fuel economy, acceleration level, response to driver commands, start time, all-weather and altitude operation, etc.

d. Research directed toward increased safety in handling liquid hydrogen by untrained persons at the service station.

8.3 CURRENT STATUS

8.3.1 Production Rates

World hydrogen production in 1965 was estimated at 2.7 trillion cubic feet (7.170 million short tons), of which two-thirds was used in manufacturing ammonia.

The U.S. Department of Commerce, Bureau of the Census, reported the following annual U.S. production figures for hydrogen, in billions of cubic feet:

Grade	1959	1960	1961	1962	1963	1964
High Purity (99.5%+)	10.6	12.9	14.3	18.0	21.2	22.1
Low Purity (below 99.5%)	47.4	52.3	51.9	57.7	72.9	85.2

These production figures did not include hydrogen produced and consumed in the manufacture of ammonia or methanol, or hydrogen produced and consumed in oil refining.

The largest single production and use of hydrogen is in ammonia manufacture. Ammonia production in the U.S. was estimated at 8.6 million short tons in 1965 (Ref. 8-8), which required the use of 602 billion ft^3 of hydrogen. World ammonia production was estimated at 25.7 million short tons, requiring 1.8 trillion ft^3 of hydrogen, or about two-thirds of the total world production of hydrogen (Ref. 8-9).

The second largest use of hydrogen is in petroleum-refining operations. This use has grown rapidly in recent years. Five hydrocracking processes (catalytic cracking with simultaneous hydrogenation) were in use in the U.S. in 1965 with an estimated annual hydrogen requirement of 63 billion ft^3 (Ref. 8-10). More than twelve hydrogen treating processes (hydrodesulfurization, etc.) were being used in the U.S. in 1965, with a hydrogen requirement of about 300 billion ft^3 per year.

A considerable portion of the hydrogen used in the preceding oil-refining processes was obtained as a by-product from catalytic hydrocarbon-reforming processes, of which more than ten were being used in the U.S. in 1965, with a total hydrogen production of about 720 billion ft^3 per year. A large portion of this by-product hydrogen was being used as fuel gas, with the remainder being utilized in oil-refining processes or ammonia synthesis.

Methanol production required about 70 billion ft^3 of hydrogen in the U.S. in 1965. A comparison of the U.S. hydrogen utilization rates in 1945 (Ref. 8-11) and 1965 appears in Table 8-4.

8.3.2 Uses

The United States space exploration program has created a large demand for hydrogen, both as a primary rocket fuel for combustion principally with oxygen and as a propellant for nuclear-powered rocket research. The production capacity of 160 tons per day of liquid hydrogen was generated primarily for the space program requirements.

Hydrogen has been favored as a propellant for nuclear space propulsion devices, essentially because of its low molecular weight. Liquid hydrogen carried by the vehicle is vaporized and heated to high temperatures by heat from the nuclear reactor, and then ejected as the propellant. Various schemes have been devised to attain maximum fuel efficiency, including the use of liquid-solid hydrogen slush to reduce storage volume and to enhance storability.

Hydrogen has been used in many industrial processes, such as the generating power in spacecraft as just discussed, as high-temperature plasma in carrying out chemical reactions, and in reducing iron ores.

Table 8-4. U.S. Hydrogen Usage

Hydrogen Usage, billion ft^3	1945	1965
Ammonia	36	602
Oil Refining	6	363
Methanol	12	70
Other Uses	18	120
Total	72	1155

Hydrogen was formerly used in large quantities for inflating lighter-than-air (LTA) vessels such as dirigibles, balloons, etc. In recent years, helium has been used for this service, whenever available, as it is nonflammable and thus safer than hydrogen. Considerable quantities of hydrogen were used in England during World War II for the inflation of barrage balloons.

Hydrogen is used in welding metals due to the intense heat of the oxygen-hydrogen flame. More recently, hydrogen has been replaced somewhat by acetylene for this purpose, although many special applications still require the use of hydrogen. Atomic-hydrogen welding is of considerable importance in welding thin sections of alloy material. In this process, hydrogen gas is passed through an electric arc between tungsten electrodes where it dissociates to atomic hydrogen. Molecular hydrogen reforms a short distance from the arc with the evolution of intense heat.

The reducing property of hydrogen is widely used in the metallurgical field. It may be used in the direct reduction of metallic oxides as in the production of tungsten and molybdenum, and the reduction of iron ore to sponge iron, as mentioned previously. In the production of metallic magnesium with carbon, the carbon monoxide and magnesium vapors leaving the furnace are chilled with a blast of hydrogen to prevent the reverse reaction, which takes place on slow cooling. Metals are bright,annealed in an atmosphere of hydrogen and/or nitrogen. This atmosphere prevents the formation of metallic oxides during the annealing operation, which would otherwise dull the surface.

Another major use of hydrogen is in the hydrogenation of vegetable and animal oils and fats to produce vegetable shortening, margarine, lard flakes, etc. Other oils are hydrogenated for use in soap and lubricants, as well as in the paint, varnish, and textile industries. Organic chemicals are also hydrogenated industrially in processes such as the production of glycols from aldols, alcohols from esters and glycerides, amines from nitriles, and cycloparaffins from aromatics. Gasoline and fuel oil may be obtained by the hydrogenation of coal, but at present this process is not competitive with obtaining these products from petroleum.

8.3.3 Consumers Costs

The cost of electrolytically produced gaseous hydrogen is a strong function of the cost of electricity, the latter presently being about $0.012/kW-hr in the United States (Ref. 8-12). a gaseous hydrogen cost of $4.60 per million Btu is given in References 8-2, 8-16 for electricity at $0.08 per kW-hr; a cost range of $3 to $5 per million Btu is given in Reference 8-13. For comparison, gaseous hydrogen from natural gas, by far the largest current source in the United States, costs $0.80 to $1.00 per million Btu (Refs. 8-2, 8-14). However, hydrogen for automotive use would probably be in the liquid state, and would be produced from coal because of natural gas shortage. The projected cost of hydrogen from coal is $2.60 per million Btu, and the additional cost of liquefaction, distribution, and retailing is estimated at $7.30, bringing the total cost at the station (without tax) to $9.90 per million Btu (Ref. 8-16).

For comparison, gasoline from petroleum currently cost $2.15 per million Btu ($0.38/gal.) at the refinery in mid-1973 (Ref. 8-16). To this figure must be added about $1.00 per million Btu ($0.115/gal) for distribution costs to the consumer (excluding taxes).

8.4 PROJECTED STATUS

8.4.1 Availability

Many possible alternatives are available for manufacturing hydrogen. Processes currently available include production from fossil fuels and water electrolysis. The source of hydrogen is either from water or hydrocarbon. Although it is theoretically easy to obtain hydrogen from coal, the process is less efficient than processes for producing hydrocarbon gas or liquids. Consequently, the more practical way would be to produce hydrogen by water electrolysis, which requires electrical power. With the optimistic assumption for a rapid nuclear buildup, it was estimated in Reference 1-2 that the maximum production of fuel hydrogen that could be accomplished in the year 2000 would be equivalent to 1.5 million barrels of petroleum per day. This would satisfy approximately 20 percent of the 1973 automobile fuel consumption, and a considerably lower percentage of the figures projected for the year 2000.

Thus, it appears unlikely that hydrogen will become a significant factor, at least for automotive application.

8.4.2 Projected Consumer Costs

A preliminary cost analysis for hydrogen produced from nuclear power (by electrolysis) and from coal is given in Reference 8-16. In the former case, a cost of $4.65 per million Btu is derived for gaseous hydrogen at the production plant, based upon power at one cent/kW-hr and a relatively high cell efficiency of 76 percent. Other sources (e.g., Ref. 8-2) arrive at somewhat lower costs ($4.50 per million Btu and up) depending upon the level of technology assumed, electrical costs, by-product credits, etc. Gaseous hydrogen from coal is projected to cost $2.60 per million Btu using improved gasification technology (Ref. 8-16).

To arrive at consumer costs for the final fuel product, here considered to be liquid hydrogen, several other items must be added. For electrolytic hydrogen an increment of $5.60 per million Btu must be added to cover. The total consumer cost is then $10.25 per million Btu. In the case of hydrogen from coal, the distribution costs may be higher because of higher liquefaction and transportation cost, resulting in distribution cost of $7.30/million Btu (Ref. 8-16).

Note that no estimated costs are given for liquid hydrogen derived from oil shale. Although this approach is technically feasible, the fact that synthetic crude oil can be more easily and cheaply obtained from shale will probably reserve this resource only for hydrocarbon fuel production, leaving water electrolysis as the most practical future source.

8.4.3 Capital Costs and Timing Implications

To have a noticeable impact on energy or pollution problems in the next 5 to 10 years, any suggested changes to fuel systems must be relatively simple and must be able to use much of the existing equipment. Past problems in handling cryogenic liquids and compressed gases will act as a deterrant to near-term use of hydrogen in any significant quantities.

When appraising capital costs for a hydrogen economy, factors to consider include the production process and the distribution systems.

Substantial savings in capital cost investment can be realized if present distribution systems for gasoline can be utilized. Unfortunately, this is not feasible, and future hydrogen-production centers will probably be located away from existing gasoline-production centers. This is because water sources and electrical power sources for hydrogen production will not likely be located near existing gasoline-producing centers.

Recent studies were conducted of capital cost investment for large-size plants for the production of hydrogen. For a 2,500-ton per day capacity, a coal conversion plant was estimated to cost $1.2 billion, as compared to $2.7 billion for a nuclear electrolysis plant. The itemized cost is shown in Table 8-5.

Table 8-5. Investment for 2,500-Ton/Day Liquid Hydrogen Supply System (Ref. 8-4)

Coal Conversion Process		Investment $ Million
Coal Requirements	31,000 tons/day, (12,000 Btu/lb), 31,000 MM Btu/hr	
Coal Conversion Plant	4 – 400 Million ft^3/day H_2 gas generators - eff. = 0.53	$ 500
Pipeline – H_2 Gas	1 – 300 Mile, 36 in. dia., 900 psi	147
Compressor Stations	2 – 12,000-hp ea, gas drive	3
Refrigeration/ Air Compression	10 – 125,000 kW – steam drive eff. = 0.65	250
Oxygen Generators	10 – 1200 tons/day cold boxes................	50
H_2 Liquefiers	10 – 250 tons/day cold boxes	100
H_2 Storage Tanks	10 – 12,500,000-gallon flat bottom tanks	63
Distribution Area	5 – Filling stations per tank	5
	Total Investment	$1,118 Million
Nuplex – Electrolysis Process		
Nuclear Energy Requirements	6,200 Megawatts, 64,000 MM Btu/hr	
Nuclear Plants	6 – 1033 MW Reactors – eff. = 0.33	$2,188
Destination Plant	6 – 1 million gallon/day units	5
Electrolysis Units	6 – 175 MM ft^3/day H_2 – 820,000 kW ea. train, 1 atm pressure	220
Refrigeration Compressors	10 – 125,000 kW – electric drive	125
H_2 Liquefiers	10 – 250 tons/day cold boxes	100
Barges – H_2 Liquid	8 – 1,100,000 gallon barges, 1-day turnaround	20
H_2 Storage Tanks	10 – 12,500,000-gallon, flat-bottom tanks.........	63
Distribution Area – Docks	....	15
	Total Investment	$2,736 Million

8.4.4 Factors Which May Inhibit Use

Technical problems of compatibility of storage containers and distribution systems must be resolved. Hydrogen embrittlement must be considered in the service life of the designs. Storage on-board and safety in handling both gaseous and liquid hydrogen is of concern. The economic impact in changing over from gasoline-fueled engines to hydrogen-fueled engines will undoubtedly be a major factor to be considered.

On a dollar-per-Btu basis, liquid hydrogen cost to the consumer will be much greater than the cost of gasoline or distillate from coal, depending upon the source of the economic analysis. Significant cost items are connected with the liquefaction of the hydrogen and its subsequent transportation and storage to retail outlets.

Technically it is easy to use coal to make hydrogen. Indeed, most synthetic fuel processes use this route to "correct" the unfavorable C:H ratio in coal. However, a more efficient use of the energy in coal is obtained as the consumption of process hydrogen is minimized. Thus, the manufacture of a hydrogen fuel product is an inefficient way of using coal energy (Ref. 8-14).

The practicality of using hydrogen as fuel, subject to the above efficiency considerations, appears to lie in the application of nuclear energy to dissociate water. Here, the problem is in the rate at which nuclear capability can be developed. Slippage in on-line dates is still continuing, and this has caused groups such as the AEC, Atomic Industrial Forum (AIF), and the staff of the Joint Committee on Atomic Energy to revise earlier downward estimates of future capability. In consequence, the time at which a "spare" nuclear capability may be conceptualized as being potentially available for hydrogen production continues to move farther into the future (Ref. 8-14).

8.4.5 Critical Technology Gaps

Research and development efforts are required before hydrogen can be considered as an alternative fuel for automotive applications. These are identified as follows:

a. Investigate economics of hydrogen production methods for large-scale use in the transportation sector

b. Develop techniques for long-distance transmission and bulk storage of hydrogen

c. Develop techniques for safe storage arrangements on-board of vehicles

d. Develop public safety guidelines and regulations.

The major obstacle to using hydrogen on a large scale is one of economics. Extensive and long-range R&D programs, as well as availability of nuclear-derived electrical energy for water electrolysis, may possibly lead to a narrowing of the gap between the cost of hydrogen and the cost of fossil fuel.

8.4.6 Potential for National and Regional Use

With overall logistics in view and, in particular, examining the problems associated with distribution of hydrogen fuel and vehicle services, any progress in conversion from hydrocarbon to hydrogen fuel must take place over a long period. Perhaps the logical place to initiate hydrogen as a fueling standard would be in new, unprecedented applications, such as projected high-speed ground transportation units. These would have the assumed advantage of a minimum of required fueling points, where trained personnel and adequate equipment could be located.

Next in turn might be conventional vehicles, such as intercity and urban trucks and city buses. Once again controlled central servicing centers are normally used, with the vehicles carrying enough fuel for extended endurance. Probably the last place that hydrogen will be put into service will be the private automobile, since it requires a very large number of service stations attended by relatively unskilled personnel. Nevertheless, such a service station operation can be conceived and, in time, an unskilled operator may be able to service hydrogen vehicles safely and efficiently. The routine servicing of LNG (essentially cryogenic methane) into a number of city fleets of "clean air" cars testifies to this potential.

Liquid hydrogen has been investigated for use as an aircraft fuel, and the Apollo program has provided significant technology to meet high standards of safety and performance. Careful overall system planning, however, will be required to convert from the present hydrocarbon fuel to a hydrogen fuel.

Using optimistic assumptions concerning a rapid buildup of post-1985 nuclear capability, it is estimated that the maximum quantity of fuel hydrogen that could be produced in the year 2000 is equivalent to 1.5 million barrels per day of petroleum. This quantity is based on the assumption of a "maximum" nuclear program and the dedication of all nuclear capability in excess of current AEC estimates to the production of hydrogen. These are considered to be unrealistic assumptions. Even so, the hydrogen-fuel potential so calculated would not be able to satisfy more than a small percentage (about 9%) of automotive fuel demand in the year 2000* (Ref. 8-14). Based on these estimates, it would appear that the more obvious potentials for nuclear energy and nuclear-derived hydrogen are to:

- Release petroleum and other fossil fuels from power generation, thereby making them available for other uses including automotive fuels
- Provide hydrogen for conversion processes (particularly, but not exclusively, coal) so as to maximize the yield of useful synthetic fuels from a given quantity of the resource processed
- Possibly supply hydrogen for a long-distance, supersonic airplane.

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*It is also possible to consider hydrogen produced by a thermochemical dissociation process. Barring a breakthrough in new decomposition cycles, it is unlikely that this approach will lead to large quantities of economical hydrogen in the next 20 years.

SECTION 9

AMMONIA

9.1 CHARACTERIZATION

9.1.1 Fuel Type

Anhydrous ammonia is a colorless gas at standard conditions with the chemical formula NH_3. At 70°F, ammonia will become a liquid when pressurized to 129 psia with a density of 38 lb/ft^3. The molecular structure of ammonia is a triagonal pyramid with an H-N-H bond angle of 107° and an N-H bond length of 1.008 angstrom (gas) and 1.13 angstrom (solid) (Ref. 9-1). Ammonia burns readily in oxygen but its combustion in air is more difficult. In the presence of a catalyst its combustion in air is aided.

On heating to 900°F or above in the presence of a catalyst, ammonia is decomposed into hydrogen and nitrogen. The decomposition of ammonia is sometimes used as a source of hydrogen, as in portable welding outfits, because a given volume of liquid ammonia will yield more hydrogen than will an equal volume of compressed hydrogen gas (Ref. 9-2).

Ammonia is under consideration as an alternative automotive fuel for storing hydrogen in nitrogen hydride form on-board a vehicle without many of the problems associated with storing pure hydrogen. Additionally, the products of combustion will contain neither carbon monoxide nor unburned hydrocarbons; oxide of nitrogen, however, will be present.

Basically, ammonia is produced by catalytic synthesis from hydrogen and nitrogen. The manufacture of ammonia therefore resolves itself into obtaining hydrogen by the methods discussed under Methods of Manufacture, Section 8.1.3, and obtaining nitrogen from air.

9.1.2 Raw Material Sources

Raw materials which lend themselves to ammonia manufacture are identical to hydrogen manufacture with the exception of the air required to provide nitrogen. Practically all current production is from natural gas or petroleum derivative sources. The nonpetroleum or natural gas derivative chemical feedstocks considered most suitable for ammonia process hydrogen manufacture are coal and oil shale. Other methods used to produce hydrogen, such as water electrolysis, can also be used. This last method is especially suitable if alternative uses for the simultaneously derived oxygen can be found. Other elements involved as a part of the processing are water, catalysts, CO plus CO_2 absorbing chemicals, electrical power, and heat, as will be discussed under methods of manufacture.

9.1.3 Methods of Manufacture

9.1.3.1 Hydrocarbon Synthesis

Most current industrial processes for the manufacture of ammonia are similar to the process shown in Figure 9-1.

The process is adaptable to produce ammonia from any gas containing hydrocarbons with the primary objective of producing free hydrogen to combine with nitrogen supplied by air. Ammonia is produced by passing hydrogen and nitrogen at elevated pressure and temperature over an iron-base catalyst (Haber process). The chemical reaction is expressed as:

$$N_2 + 3\,H_2 \xrightarrow{\text{Catalyst (Iron Alloys)}} 2\,NH_3$$

Gases leaving the catalytic converter are cooled to condense the ammonia, which is removed as a liquid.

The process operates in the following manner: A portion of the hydrocarbon in the feedstock is converted to raw synthesis gas, combining with steam in the primary steam reformer to form H_2 and CO. The remaining hydrocarbons are converted in the secondary reformer. Air is introduced to supply nitrogen. The CO shift converter catalytically oxidizes most of the CO to CO_2. After cooling, the major portion of the CO_2 is removed by chemical reactions. The residual CO and CO_2 are then removed by methanation.

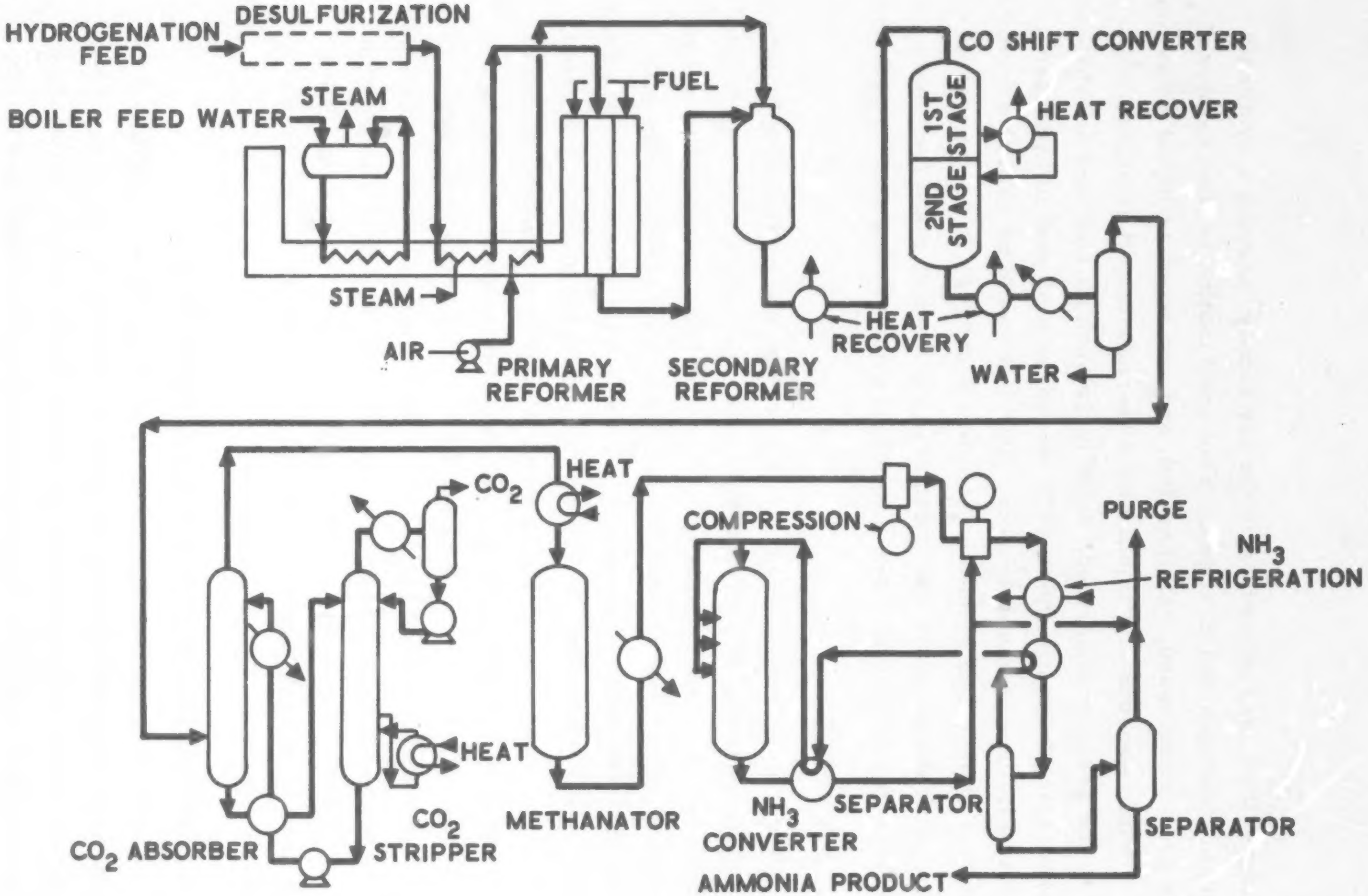
HYDROGENATION FEED
DESULFURIZATION
BOILER FEED WATER
STEAM
FUEL
STEAM
AIR
PRIMARY REFORMER
SECONDARY REFORMER
CO SHIFT CONVERTER
1ST STAGE
2ND STAGE
HEAT RECOVER
HEAT RECOVERY
WATER
HEAT
CO_2
HEAT
CO_2 ABSORBER
CO_2 STRIPPER
METHANATOR
COMPRESSION
NH_3 CONVERTER
SEPARATOR
PURGE
NH_3 REFRIGERATION
SEPARATOR
AMMONIA PRODUCT

Figure 9-1. Ammonia Synthesis from Natural Gas or Naphtha (Ref. 9-3)

The process described uses up oxygen in the air supply, leaving a synthesis gas consisting of hydrogen and nitrogen. This combination is then catalyzed into ammonia gas, compressed, refrigerated, and extracted as liquid ammonia.

While gaseous and liquid raw materials lend themselves relatively easily to the process described, solid fuels such as coal and oil shale require preprocessing to gasify them. The conversion of coal to hydrogen is briefly covered in the preceding section. Nitrogen would be obtained from an air liquefaction plant. The remaining synthesis process is as just described. However, with the possible exception of a combustion plant (see Section 9.1.3.3), it is unrealistic to make ammonia by converting coal to hydrogen.

9.1.3.2 Electrolysis

The two principal electrolytic processes for producing hydrogen, water, and hydrogen halide electrolysis were discussed under hydrogen production methods. Current installed electrolysis plant capacity throughout the world is estimated to be three million pounds of hydrogen per day with primary use in the production of ammonia. This is only 3 percent of the daily U.S. hydrogen consumption (Ref. 9-4). The electrolysis plants are located where there is significant demand for ammonia-derived fertilizer, plentiful low-cost electricity, and no low-cost hydrocarbon fuel supply such as in India, Egypt, Chile, Norway (Ref. 9-4), and British Columbia in Canada (Ref. 9-5). As previously noted, the manufacture of nitrogen for the catalytic synthesis of the ammonia requires an air liquefaction facility. The by-product of both water (or halide) electrolysis and air liquefaction is oxygen. Since oxygen can be used in the synthesis of hydrogen from coal, the concept of a combined system approach appears attractive.

9.1.3.3 Combination Hydrocarbon/Electrolysis System

Figure 9-2 derived from Reference 9-4 shows a combined system whereby coal is gasified using an oxygen gasification system. The required oxygen would be supplied from the electrolysis and air separation systems. The hydrogen produced by the combined hydrocarbon gasification and electrolysis would then be converted into ammonia by catalytic synthesis with the nitrogen produced by the air separation facility.

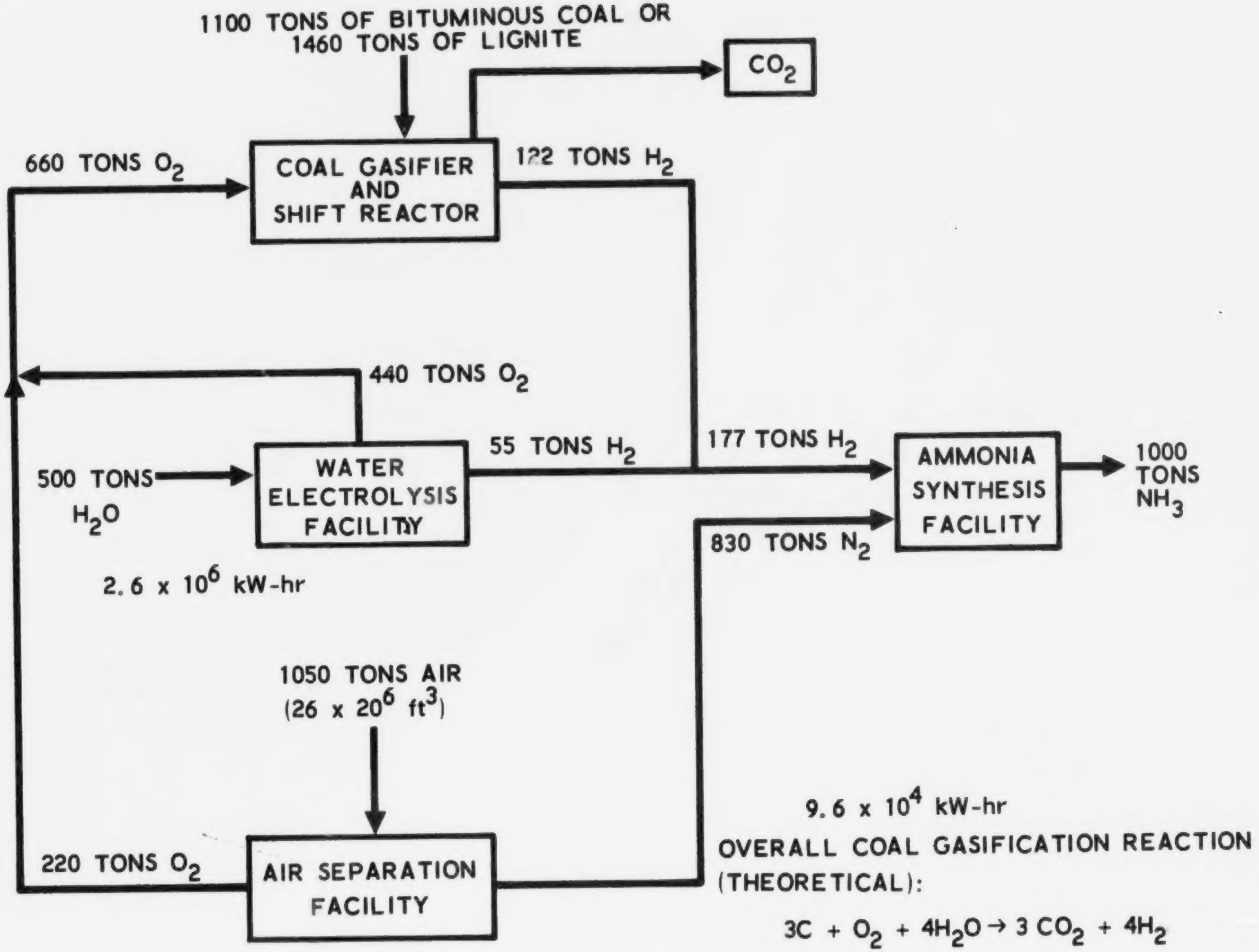
1100 TONS OF BITUMINOUS COAL OR
1460 TONS OF LIGNITE
CO_2
660 TONS O_2
COAL GASIFIER AND SHIFT REACTOR
122 TONS H_2
440 TONS O_2
500 TONS H_2O
WATER ELECTROLYSIS FACILITY
55 TONS H_2
177 TONS H_2
AMMONIA SYNTHESIS FACILITY
1000 TONS NH_3
830 TONS N_2
2.6 x 10^6 kW-hr
1050 TONS AIR
(26 x 20^6 ft^3)
220 TONS O_2
AIR SEPARATION FACILITY
9.6 x 10^4 kW-hr
OVERALL COAL GASIFICATION REACTION
(THEORETICAL):
$3C + O_2 + 4H_2O \rightarrow 3\,CO_2 + 4H_2$

Figure 9-2. Combined Coal Gasification/Water Electrolysis (Ref. 9-4)

9.1.3.4 Summary of Ammonia Manufacture

Table 9-1 provides a summary of the ammonia manufacturing processes, including energy and raw material resources data from Refs. 2-1 and 9-4. The thermal efficiencies of the various processes are based on the ratio of gross calorific values of the ammonia produced to the total process equivalent heat input. For processes using large amounts of electrical power, the efficiency of the electric power generation process was included. The efficiencies using synthetic liquid or gaseous fuels as raw materials do not include the efficiency in producing them from coal or shale.

9.1.4 Physical and Chemical Properties

The physicochemical properties of anhydrous ammonia are provided in Table 9-2. It can be noted that the net heating value of ammonia is 8000 Btu per pound compared to heating value of 19,000 Btu per pound for gasoline. This indicates that, for equal combustion efficiencies, approximately 2.4 times the amount of ammonia as gasoline is required for equal energy outputs.

The vapor pressure of liquid ammonia ranges from 250 psia to 20 psia over the normal automotive temperature extremes of 110°F to -20°F, respectively. This indicates that the vehicle storage tank should pressurize the ammonia to approximately 250 psia to maintain the ammonia in liquid form. The flammability characteristics of ammonia in air and oxygen at atmospheric pressures are shown in Figure 9-3.

9.2 SUITABILITY FOR USE AS AN ENGINE FUEL

As noted previously, the interest in ammonia as an engine fuel stems from the consideration that it allows the storage of hydrogen in nitrogen hydride form at relatively low pressures (250 psia) when at ambient temperatures. Additionally, the products of combustion will contain neither carbon

Table 9-1. Ammonia Production

Energy/Material Resources	Name of the Process	Comment on the Process	Synthesized Fuel	By-Product	Thermal Efficiency %[a]	Comments on Pollution	Reference
Coal to Ammonia							
1.8 ton coal 147 kWhr 6600 lb boiler feed water 490,000 cooling water catalysts	Make H_2 by any process, then make ammonia	Requires 44.05 million Btu/1 ton NH_3	1 ton of ammonia	--	44	Sulfur removal problems are similar to coal gasification problems.	2-1
Coal or Oil Shale Derived Light Naphtha to Ammonia							
0.81 tons naphtha 33.5 kWhr 6180 lb boiler feed water 468,000 lb cooling water	Gasify naphtha to produce H_2 and then make ammonia	Requires 33.7 million Btu/1 ton NH_3	1 ton of ammonia	--	57[b]	Sulfur removal is necessary for feedstocks containing sulfur.	2-1
SNG to Ammonia							
32.6 million Btu of SNG as feed and fuel. 15 kWhr 22,400 lb makeup water	Reform SNG to make H_2 and then make ammonia	Requires about 32.9 million Btu/ton of NH_3	1 ton of ammonia	--	59[b]	Minimum pollution problems	2-1
Coal or Oil Shale-Derived Heavy Oil to Ammonia							
0.94 tons heavy oil, 110 kWhr 3840 lb. boiler feed water 883,000 lb cooling water	Gasify to produce H_2 and then make NH_3	Requires about 36.9 million Btu/ton of NH_3	1 ton of ammonia	--	53[b]	Sulfur removal problems are similar to coal gasification problems.	2-1
Water Electrolysis to Ammonia							
1.61 tons Distilled or demineralized H_2O 1.05 tons air, 85 tons cooling water, catalysts		7750 kWhr	1 ton of ammonia	oxygen	25[c]	Thermal pollution sulfur removal	9-4, 2-1
Combination Coal Gasification/Electrolysis							
1.1 tons coal or 1.5 tons Lignite 0.5 tons distilled water 1.05 tons air 2600 kWhr 0.4 tons feed water 26.4 tons cooling water, catalysts			1 ton of ammonia	--	38[d]	Sulfur removal thermal pollution	9-4, 2-1

[a] Thermal efficiency based upon higher heating value of input and product streams.

[b] Does not include energy involved in producing liquid or gaseous hydrocarbon raw materials from coal or shale.

[c] Assumes 33% thermal efficiency to produce electricity, 75% efficiency to electrolize water.

[d] Assumes 29% thermal efficiency to electrolize water, 44% thermal efficiency to gasify coal.

Table 9-2. Physiochemical Properties of Anhydrous Ammonia (Ref. 2-1)

Chemical Formula	NH_3
Molecular Weight	17.031
Melting Point	-108°F
Normal Boiling Point (NBP)[a]	-28°F
Density at Normal Boiling Point	
Vapor, lbs/ft^3	0.0556
Liquid, lbs/ft^3	42.6
Density at 70°F	
Vapor, lb/ft^3	0.0433
Liquid, lb/ft^3	38.0
Heating Value, Liquid	
Lower Heating Value, Btu/lb	8,000
Lower Heating Value, Btu/gal (70°F)	40,640
Products of Combustion, Liquid	
Heat of vaporization at NBP, Btu/lb	591
Flammable limits in air, vol %	16-27
Autoignition temperature, °F	1204
Stoichrometric mixture, lb air/lb fuel	6.1
Research octane number	130

[a] At atmospheric pressure of 14.7 psia.

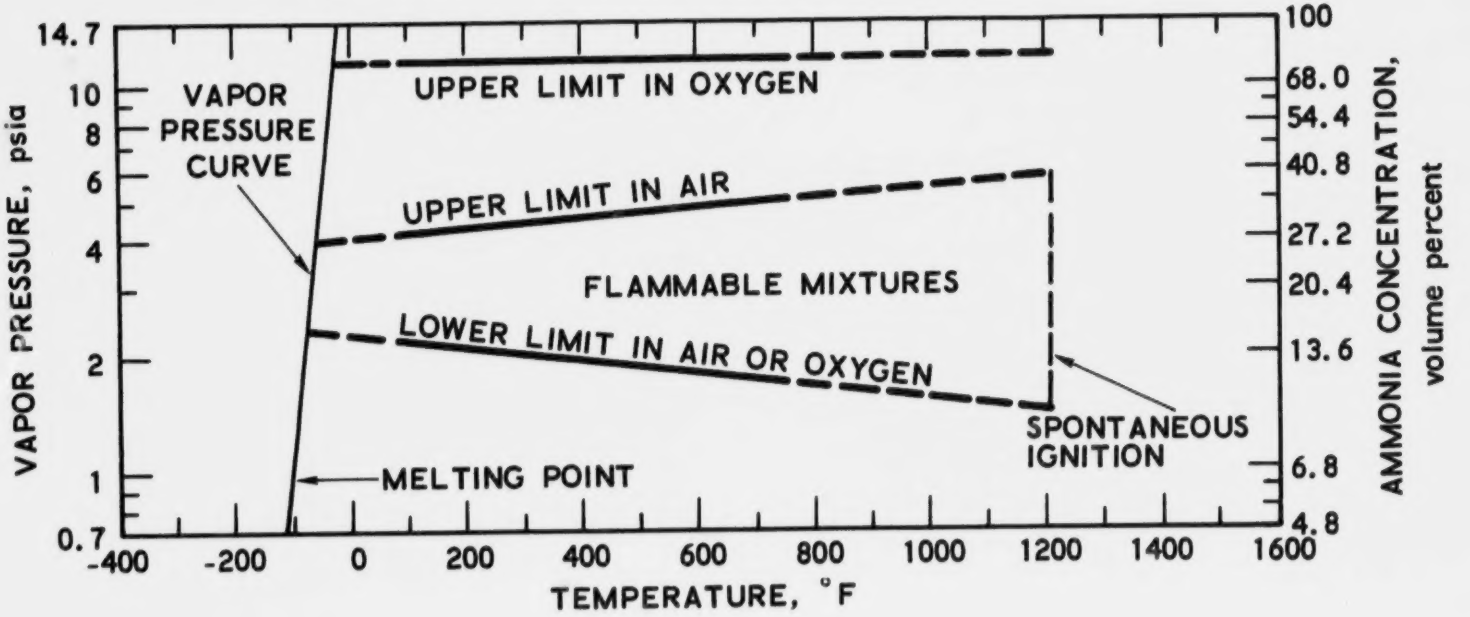

Figure 9-3. Flammability Characteristics of Ammonia in Air and Oxygen at Atmospheric Pressure (Ref. 9-6)

monoxide (CO) nor unburned hydrocarbons (HC), two automobile exhaust pollutants of current concern. Oxides of nitrogen will be present, however. The following discussion addresses:

- The use of ammonia as a fuel for various automotive heat engines
- The exhaust emissions including nitric oxides (NO_x) and unburned NH_3
- The requirements to handle, store, and distribute the ammonia fuel considering toxicity and safety requirements
- The fuel economy effects.

The characteristics of ammonia as a fuel applicable to any engine are noted below. Of particular note are emission effects where NO_x and unburned NH_3 in the exhaust represent potential air pollution problems. The impact of ammonia as a fuel for the typical automobile engine is also noted below. For a convenient frame of reference, the data are normalized to the use of a hydrocarbon fuel, gasoline.

- Otto Cycle Engine. Data are available for the use of ammonia as a fuel for conventional reciprocating engines but not for rotary or stratified charge engines. Since these are versions of an Otto cycle engine, however, it is expected that the general trends for the typical automotive reciprocating engine will apply to them as well.
- Gas Turbine Engine. There are minimal data available on the use of ammonia as a fuel for gas turbine engines. Most of the available data are based on theoretical predictions (Refs. 9-7 and 9-8) and are shown below.
- Diesel Engine. The impact of using ammonia fuel for Diesel engines is indicated in the following paragraphs. The data are indexed to cetane as the HC fuel and are mainly based on experimental results (Ref. 9-9).
- External Combustion Engines. No data are available for the use of ammonia as a fuel for Rankine and Stirling engines. However, based on the smaller (8000 Btu/lb) content of ammonia, fuel consumption would be more than twice that of gasoline. Additionally, the potential pollution from NO_x and unburned NH_3 in the exhaust would present problems.

9.2.1 Engine Compatibility

Ammonia is corrosive to copper, zinc, and their alloys (Ref. 9-3).

- Otto Cycle Engine
  - Spark Advance: 54° for NH_3 vs 30 to 43° for HC fuel for maximum output. The greater advance is considered to be due to a flame-propagation rate about 30% slower and a kernel development time 40% longer for NH_3 (Ref. 9-10).
  - Cooling Jacket Temperature: 354°F for NH_3 to enhance decomposition during compression versus 152°F for HC fuel to suppress knocking at a compression ratio of 10.
  - NH_3 Dissociation: 4 to 5% H_2 needed to obtain maximum engine power at any given mixture ratio at 1800 rpm and a compression ratio of 8. About 25% of the NH_3 must be dissociated to achieve 4 to 5% of H_2.
  - Peak Power: 65 to 71% of HC fuel peak power for operation on NH_3.
- Gas Turbine Engine*
  - Power Output: Ammonia can yield power output up to 10% greater than that for hydrocarbon fuels under the same conditions of limited turbine inlet temperature. This is due to the combined effects of high heat of vaporization and high yield of product moles for ammonia.
  - Thermal Efficiency: Ammonia efficiencies should range up to 10% higher than with HC fuels due to the high yield of product moles.
  - Combustion Stability Limits: Blowout points are characterized by low frequency pulsations (1/2-1 Hz). Addition of 5% propane will suppress pulsation and more than double the maximum blowout limits.
- Diesel Engine
  - Ignition: A compression ratio of 35 to 1 or higher would be required for compression ignition of NH_3.

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* Minimum data available, mostly based on theoretical predictions (Refs. 9-7 and 9-8)

- Fuel Injection: NH_3 injection at 150 - 180° before top dead center (btdc) versus 10° btdc for diesel fuel.
- Combustion Chamber Peak Pressure: 750 psi for NH_3 vs. 1000 psi for diesel fuel.
- Peak Power: At a comparable fuel-air equivalence ratio, the engine develops about 10% less power on liquid NH_3 than on diesel fuel. However, diesel-fueled engines are usually smoke limited to operate at a fuel-air equivalence ratio of 0.7, whereas NH_3 peak power is developed at an equivalence ratio of 1.06. Compared this way, the NH_3 fueled engine will produce about 20% more power.

9.2.2 Emission Effects

Nitric oxide concentrations in excess of calculated equilibrium levels were observed over the fuel-air equivalence-ratio range of 0.4 to 1.85 in ammonia combustion in an atmospheric pressure flame and are considered likely to be of concern to air pollution (Ref. 9-11).

In the same experiment, the measurement of unburned ammonia led to the conclusion that utilization of NH_3 as a fuel is likely to result in the production of unburned NH_3 at levels which must be of concern to air pollution.

- Otto Cycle Engine (Ref. 9-12)
  - HC: There are no hydrocarbon emissions for NH_3 fuel.
  - CO: There are no carbon monoxide emissions from NH_3 fuel.
  - NO_x: The nitric oxide emissions for NH_3 are 3.8 times those of HC fuel at maximum power output. At maximum economy, the NH_3 emissions are 1.5 times those of HC fuel.
  - NH_3: (No data)

- Gas Turbine Engine (No data)
- Diesel Engine (No data)

9.2.3 Fuel Economy

- Otto Cycle Engine. Specific Fuel Consumption (SFC) for NH_3 is approximately 2.4 times that of hydrocarbon fuel at maximum economy.
- Gas Turbine Engine. The SFC for ammonia is predicted to exceed that of hydrocarbon fuels by 2.5 to 3 times.
- Diesel Engines. The SFC for NH_3 is about 2.4 times that of diesel fuel over wide operating ranges of fuel-air ratios and compression ratios.

9.2.4 Toxicity Effects

The physiological effects of ammonia are directly traceable to its ability to produce local severe irritation of tissues (Ref. 9-13). Ammonia is extremely irritating and highly corrosive to the eyes and respiratory tract. Suffocation and death from pulmonary edema can result from exposure to high concentrations. The threshold limit value for ammonia is 50 ppm, the same as for carbon monoxide. Thus, ammonia is highly toxic. The irritant properties and pungent odor give adequate warning so that toxic exposures are not voluntarily permitted. Up to 500 ppm in air may be tolerated for an hour. Irritation of mucous membranes of the eyes, nose, and throat have been reported at 400 to 700 ppm. Exposures of 2500 to 6500 ppm have been judged dangerous for 0.5 hour, and 5000 ppm and above is believed to be rapidly fatal. High concentrations of ammonia in addition to the corrosive action on eyes, throat, and respiratory tract may also reflectively affect heart and respiratory action. Moist atmospheres containing a 1 percent or more ammonia may cause increasing amounts of skin irritation including chemical burns with blistering. There is no evidence of cumulative or chronic toxic effects following prolonged or repeated exposures to tolerable atmospheric concentrations.

9.2.5 Safety Effects

Ammonia is very stable and not shock sensitive. The flammability range in air (16 to 27 percent by volume) is at higher concentrations than for gasoline, but large anhydrous ammonia spills present a fire hazard. Ammonia fires have proved very difficult to extinguish; water fog in large quantities is required.

9.2.6 Handling, Storage and Distribution Requirements

Based on fuel consumption for ammonia of 2.4 times that for gasoline, it would take 284 pounds of stored ammonia to equal 20 gallons of gasoline (119 pounds for gasoline). The NH_3 volume required is 7.16 cubic feet (versus 2.59 cubic feet of gasoline) or a volume ratio of 2.8 times. The weight of NH_3 plus a 250-psi tank is 445 pounds (versus 134 pounds for gasoline and tank) or a total weight ratio of 3.4 times (Ref. 9-13).

Based on current NH_3 storage and handling practices (Ref. 9-14), the automobile storage tank should be designed for a working pressure of 250 psia and be equipped with two relief valves. The current practices of venting to a stack which discharges at least 6 feet above any surrounding platform or work area and that of providing ventilation to avoid pocketing of ammonia under roofs, implies a requirement for an automobile to carry some form of closed capture system for containing ammonia venting. Based on current practice a closed two-line pressure differential system appears to be required for filling the automobile storage tank. The fuel transfer system in the vehicle will have to be a closed and pressurized system.

9.2.7 Critical Research Gaps

- Otto Cycle Engine
  - NO_x Emissions: The NO_x emissions measured are higher than those predicted from equilibrium calculations. Knowledge as to the NO_x formation mechanisms is needed.

    - NH$_3$ Emissions: The literature does not indicate any measurements of NH$_3$ in the engine exhaust. Since this represents a new pollution problem, such data are needed.

- Gas Turbine Engine. Experimental data appear to be needed to verify power output, thermal efficiencies, and specific fuel consumption, and to investigate improvement of combustion stability (e.g., effects of NH$_3$ dissociation) and quantification of exhaust products.
- Diesel Engine. Experimental data for quantification of exhaust products using NH$_3$ fuel appear to be needed as do data for optimizing ignition. However, NH$_3$ does not appear to be a practical fuel for this type of engine.

9.3 CURRENT STATUS

9.3.1 Production Rates

The 1971 U.S. annual production rate of synthetic anhydrous ammonia was 13 million tons (Ref. 9-15). Almost all of this was used for fertilizer materials. A relatively small amount is converted into nitric acid for other purposes. Per Reference 2-1, to drive equal distances in a conventional piston engine automobile requires on the average 2.35 times as much ammonia by weight as gasoline. As of March 1973, the daily average production of automotive gasoline at U.S. refineries was 6.128 million barrels per day (Ref. 9-16), which is equivalent to approximately 365 million tons per year. By using the factor of 2.35 to convert to ammonia usage, this would then require 860 million tons of ammonia or 66 times the current annual production rate.

9.3.2 Consumer Costs

A 1,000-ton-per-day plant on the U.S. Gulf coast using naphtha as feedstock, required a \$23 million capital investment and now produces ammonia at \$48.39 per ton (Ref. 9-16), which is equivalent to \$0.123 per gallon of ammonia (f.o.b. plant) or \$3.03 per million Btu. The estimated production cost using electrolytic hydrogen is \$6.25 per million Btu, to which a distribution cost of \$1.40 per million Btu must be added (Ref. 2-1). Thus, ammonia offers no economic advantage compared to alternative hydrocarbon or methanol fuels.

9.4 PROJECTED STATUS

9.4.1 Availability

The projected availability of ammonia is dependent on the raw materials used for its manufacture. Coal gasification or oil shale conversion to gas using humidified oxygen followed by hydrogen-nitrogen catalyzation are possible candidate processes for producing ammonia. For electrolysis of water, nuclear-derived electric power to electrolyze the water and to liquify air is the primary candidate.

9.4.1.1 Ammonia from Coal

The domestic consumption of coal in 1970 was 517 million tons (Ref. 9-17). Based on Table 9-1, 1.8 tons of coal are required to produce one ton of ammonia. In order to produce 860 million tons per year of ammonia to replace current gasoline usage for automotive use, an annual total of 1,550 million tons of coal would be required. This is approximately triple the current coal consumption and would require a total annual coal consumption in excess of 2 billion tons based on 1970 consumption rates. Although this consumption rate indicates that depletion of coal would be relatively slow, it must be considered that energy demands are consistently increasing. Reference 9-4 states that 50 percent of the world coal reserves will be depleted by the years 2030 to 2070, with nearer-term depletion if coal is used to manufacture synthetic fuel. Nevertheless, ammonia from coal shows a relatively good near-term availability.

9.4.1.2 Ammonia by Water Electrolysis

The use of nuclear-derived electrical power for water electrolysis to produce ammonia is claimed to be the most realistic method using present technology (Ref. 9-4). The availability of energy from uranium using conventional reactors has been estimated at $12,000 \times 10^{18}$ Btu (Ref. 9-18) which is equivalent to 3.5×10^{18} kW-hr. This figure can probably be expanded by more than a magnitude if fast breeder reactors are developed. Other methods of utilizing nuclear energy to produce H_2 have been studied: (1) thermal decomposition of water at high temperature, (2) radiolytic decomposition of water by fission fragments, (3) heat input to a multistep chemical process.

The production of 860 million annual tons of ammonia by water electrolysis would require 6.65×10^{12} kW-hr annually which is equivalent to an installed capacity of 7.7×10^5 megawatts. This can be compared with 1973 U.S. electrical energy installed capacity from all fuels of $\sim 3 \times 10^5$ megawatts, using 1.33×10^{12} kW-hr annually as interpolated from data in Reference 9-18. An electrical energy capacity expansion of more than double the 1973 capacity and a consumption rate of approximately five times that in 1973 would therefore be required to meet the annual demand of ammonia to replace 1973 gasoline usage. It appears that the availability of uranium using conventional reactors could satisfy this demand for long periods. It must, however, be kept in mind that electrical energy consumption due to other demands is predicted to triple by the year 2000.

The consumption of water to produce 860 million annual tons of ammonia is estimated at 1.38 billion annual tons of distilled or demineralized water to produce hydrogen. In addition to this amount consumed, 73 billion annual tons of cooling water in excess of this amount would be required for the electrolysis process. Additional cooling water would be required for nuclear reactors and electrical power plants to generate the 6.65×10^{12} kW-hr. Based on data extrapolated from Reference 9-18, it is estimated that these facilities would require 1,520 billion tons per year of cooling water for an assumed 12°F temperature rise. Makeup water requirements are normally 4 percent of the total cooling water flow with evaporation accounting for 1 to 1-1/2 percent and blowdown for 2 to 3 percent (Ref. 9-18). For an assumed evaporation loss of 1-1/4 percent, the evaporation consumption would then be ~19 billion tons per year, and the total makeup withdrawal would be approximately sixty billion tons per year. This compares with a 1970 U.S. consumption of 134 billion tons per year and withdrawals of 565 billion tons per year. It can be noted that cooling water is a critical raw material to produce ammonia by electrolysis unless sea water or considerably more expensive air cooling methods are used.

9.4.2 Capital Costs

9.4.2.1 Ammonia from Coal

The capital costs for producing ammonia by coal gasification would exceed \$54 billion estimated for ammonia produced from naphtha, since coal gasification plants would be required. A 250 million cubic feet per day plant by El Paso Natural Gas will cost \$250 million (Ref. 9-19). Assuming a 35 percent hydrogen content gas, this type of plant would produce 87 million cubic feet per day of hydrogen or 83,000 tons annually. It is estimated that 860 million tons of ammonia would require 152 million tons of hydrogen or 1,800 such plants for a total cost of \$450 billion. For larger plants producing approximately 3,000 tons of ammonia per day each, it is estimated that this cost could be reduced to \$300 billion (Ref. 9-20). To this cost would have to be added the capital investment to produce 960 million tons of oxygen for the oxygen blasting of the coal and the nitrogen required for ammonia synthesis. It can be noted that the capital cost of ammonia by coal gasification would be approximately a magnitude higher than by conventional processes.

9.4.2.2 Ammonia by Water Electrolysis

The capital cost of the installed electrical capacity of 7.7×10^5 megawatts is estimated at \$230 billion based on \$300 million per 1,000 megawatts (Ref. 9-18). The capital cost of the total process will probably be higher by more than a magnitude than the more conventional means of ammonia production from natural gas or naphtha feedstocks.

9.4.3 Summary

Since coal gasification and water electrolysis, particularly the latter, are the major candidates for ammonia production in the future, the capital investment to produce ammonia by these means appears extremely high when compared to conventional processes. Reference 9-21 concluded that ammonia could be produced competitively via electrolysis with the conventional process of natural gas or naphtha conversion. However, this study assumed that electrical power would be provided by external sources and did not include the tremendous capital investment for new electrical power sources to produce ammonia in the amounts required to meet national transportation needs. In view of the many other problems associated with ammonia usage, it does not appear to be a promising alternative fuel.

SECTION 10

HYDRAZINE

10.1 CHARACTERIZATION

Hydrazine (N_2H_4) is a clear, colorless, hygroscopic liquid with an odor similar to that of ammonia. Hydrazine was first produced in the laboratory in 1887. Early use of hydrazine was in sugar chemistry, giving cystalline, easily recognizable derivatives. Today, hydrazine derivatives are used in the plastic industry, in the pharmaceutical industry and predominantly as fuel for rocket propulsion.

10.1.1 Fuel Type

Hydrazine is a strong reducing agent and will also react with carbon dioxide or air. When exposed to air on large surfaces, such as rags, hydrazine may ignite spontaneously, due to evolution of heat caused by oxidation with atmospheric oxygen. A film of hydrazine in contact with metallic oxides and other reducing agents may ignite.

Until hydrazine was used as a rocket fuel by the Germans in World War II, it had remained in the laboratory as a curiosity. Hydrazine is of great interest now as a storable propellant for rockets; in combination with a strong oxidizing agent, it is one of the highest performing chemical fuels.

10.1.2 Methods of Manufacture

The Raschig process and the urea process are closely related to those currently used commercially for the manufacture of hydrazine.

In the Raschig process, the synthesis of hydrazine from ammonia and sodium hypochlorite takes place in the following steps: Initially, chloramine is formed from ammonia and sodium hypochlorite:

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$$

Then, the chloramine reacts with excess ammonia to form hydrazine:

$$NH_2Cl + NH_3 + NaOH \rightarrow NH_2NH_2 + NaCl + H_2O$$

The formation of chloramine is rapid, whereas the reaction of chloramine with ammonia is slow and rate-determining, requiring heat.

Hydrazine, a strong reducing agent, is sensitive to a variety of oxidizing agents, particularly in the presence of metal ions. Oxidizing agents, such as chloramine, dichloramine, nitrogen trichloride, and sodium chlorate, are present in varying amounts in the reaction liquor during the formation of hydrazine. Thus, as the formation of hydrazine proceeds, chloramine may oxidize or react with hydrazine to form ammonium chloride and nitrogen.

$$NH_2NH_2 + 2\,NH_2Cl \rightarrow 2NH_4Cl + N_2$$

The rate of formation of hydrazine increases with the temperature, but the rate of decomposition is essentially independent of the temperature. Thus, it is best to run the reaction at high temperatures. At about 130°C rapid conversion of chloramine to hydrazine is ensured and, by using a large excess of ammonia (20:1 to 30:1) to react with any chloramine that is formed, the decomposition of hydrazine by chloramine is kept at a minimum. Raschig's "catalysts" increase the yield of hydrazine by complexing the metal-ion impurities that catalyze the decomposition of hydrazine by chloramine. A schematic of the Raschig process is shown in Figure 10-1.

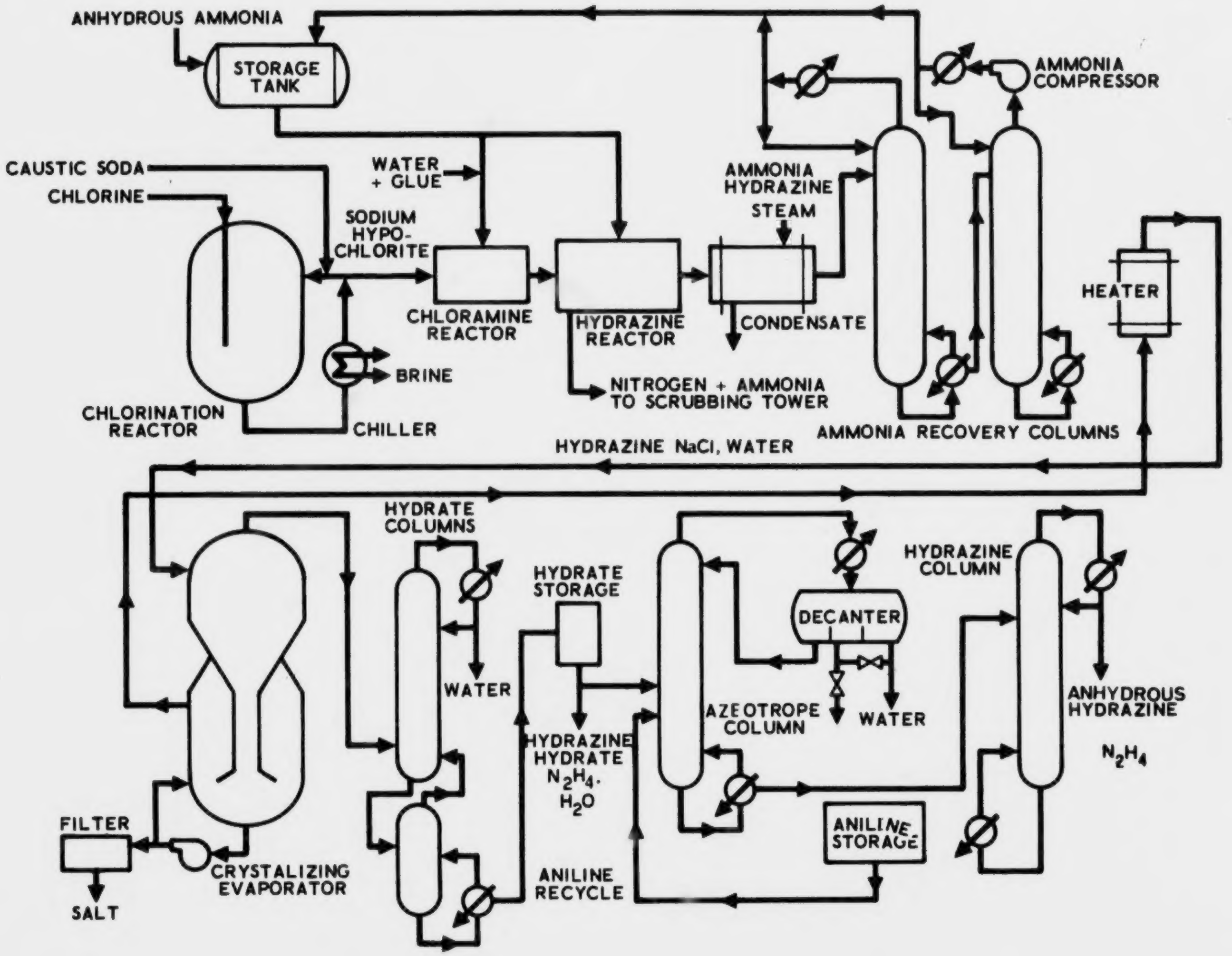
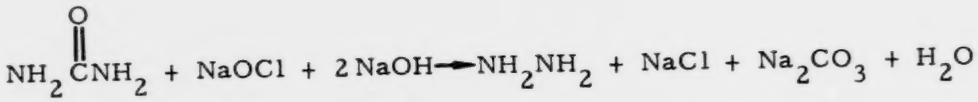

ANHYDROUS AMMONIA
STORAGE TANK
CAUSTIC SODA
CHLORINE
WATER + GLUE
SODIUM HYPO-CHLORITE
CHLORINATION REACTOR
BRINE
CHILLER
CHLORAMINE REACTOR
HYDRAZINE REACTOR
NITROGEN + AMMONIA TO SCRUBBING TOWER
AMMONIA HYDRAZINE
STEAM
CONDENSATE
AMMONIA COMPRESSOR
AMMONIA RECOVERY COLUMNS
HEATER
HYDRAZINE NaCl, WATER
HYDRATE COLUMNS
WATER
HYDRATE STORAGE
HYDRAZINE HYDRATE $N_2H_4 \cdot H_2O$
ANILINE RECYCLE
FILTER
SALT
CRYSTALIZING EVAPORATOR
DECANTER
AZEOTROPE COLUMN
WATER
ANILINE STORAGE
HYDRAZINE COLUMN
ANHYDROUS HYDRAZINE
N_2H_4

Figure 10-1. Manufacture of Hydrazine by the Raschig Process (Ref. 10-1)

The degradation of urea by sodium hypochlorite forms the basis of this process for the production of hydrazine.



$$NH_2\overset{\overset{O}{\|}}{C}NH_2 + NaOCl + 2\,NaOH \rightarrow NH_2NH_2 + NaCl + Na_2CO_3 + H_2O$$

In the urea process, a cold solution of urea and sodium hydroxide is added to a cold solution of sodium hypochlorite. The heat of reaction increases the temperature to 100° C, where the reaction takes place rapidly. As in the Raschig process, various proteins are usually added to prevent the decomposition of hydrazine.

A 43-percent solution of urea is prepared by dissolving urea in water while steam is passed through the solution to maintain the temperature at about 5° C, since the dissolution is strongly endothermic. A 30 percent solution of sodium hydroxide is chlorinated until it has an available chlorine content of 140 to 155 grams per liter and a residual sodium hydroxide content of 170 to 190 grams per liter.

These solutions (four volumes of sodium hypochlorite-sodium hydroxide to one volume of urea solution with 500 mg of glue per liter) are fed continuously to the reactor where the temperature is allowed to rise to 100°C. The reaction liquor contains approximately 35 grams of hydrazine per liter of solution; a schematic for the urea process is shown in Figure 10-2.

10.1.3 Physical and Chemical Properties

Anhydrous hydrazine is a strong reducing agent and a weak chemical base. Aqueous hydrazine shows both oxidizing and reducing properties. Although data show hydrazine to be a powerful oxidizing agent in acidic solutions, reactions with many reducing agents are so slow that only the most powerful ones reduce it quantitatively to ammonia ion. Hydrazine is an endothermic compound and will decompose spontaneously in a way

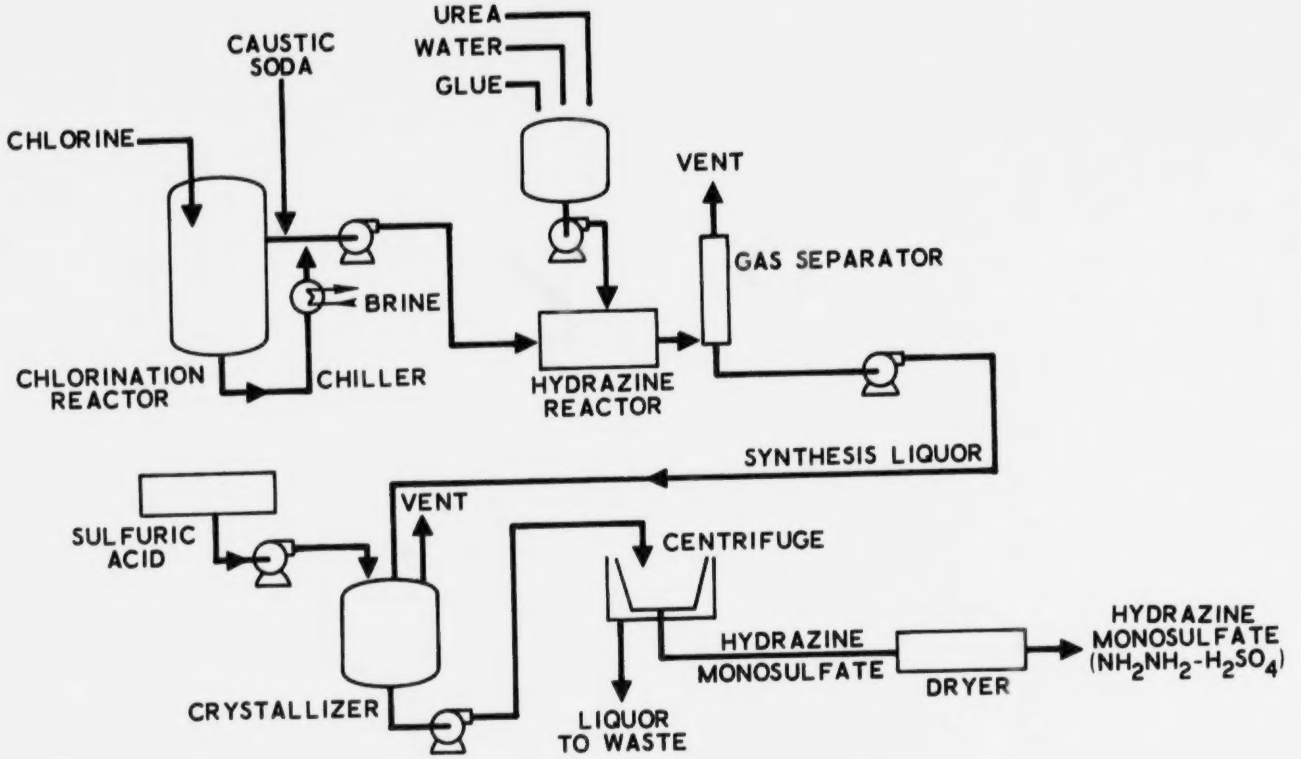

UREA
WATER
GLUE
CAUSTIC SODA
CHLORINE
VENT
GAS SEPARATOR
BRINE
CHLORINATION REACTOR
CHILLER
HYDRAZINE REACTOR
SYNTHESIS LIQUOR
VENT
SULFURIC ACID
CENTRIFUGE
HYDRAZINE MONOSULFATE
HYDRAZINE MONOSULFATE
DRYER
HYDRAZINE MONOSULFATE (NH_2NH_2-H_2SO_4)
CRYSTALLIZER
LIQUOR TO WASTE

Figure 10-2. Manufacture of Hydrazine by the Urea Process (Ref. 10-1)

similar to hydrogen peroxide. It is incompatible with many metals, plastics, and lubricants. The reaction of hydrazine with the oxide of copper, manganese, iron, silver, mercury, molybdenum, lead or chromium may be particularly violent.

Hydrazine has a molecular weight of 32.04. It freezes at 34.7°F and boils at 236.3°F. Its density is 8.482 pounds per gallon at 77°F. The heat of combustion with air is 8,346 Btu per pound at 77°F. Flammability limits in air at 68°F and one atmosphere is 4.7 percent lower and 100 percent upper by volume.

10.2 SUITABILITY FOR USE AS AN ENGINE FUEL

10.2.1 Engine/Vehicle Compatibility

No data are available. Hydrazine has heretofore not been seriously considered as an automotive fuel, although it could find application in fuel cells for electric vehicles.

10.2.2 Toxicity Effects

Anhydrous or aqueous solutions of hydrazine are toxic by ingestion, inhalation of vapors, or contact with the skin. The maximum allowable concentration of one ppm has been established by the American Conference of Governmental Hygienists. The maximum tolerable concentration in air breathed for no more than 10 minutes is suggested as 10 ppm. Hydrazine produces local irritating effects upon the eyes and respiratory tract. Inhalation causes dizziness, nausea, and possibly death. Repeated or chronic exposure causes damage to the liver. Hydrazine salts produce hyperglycema. Symptoms resulting from exposure to hydrazine include itching of the eyes and a slight swelling initially and conjunctivitis after about a day. Although hydrazine has a readily detectable ammoniacal odor, smell should not be relied on as a warning of excessive concentration because, on contact with vapors, membranes of the nose desensitize rapidly. Contact of hydrazine with any body tissue will produce a caustic-like burn if not washed off immediately.

10.2.3 Safety Effects

10.2.3.1 Fire Hazard

Liquid anhydrous hydrazine is very stable and nonexplosive. In the absence of decomposition catalysts, it has been heated above 500°F with very little decomposition. Hydrazine vapors, however, can present a hazard. Mixtures of hydrazine vapor in air are flammable between the limits of 4.7 percent and 100 percent hydrazine by volume. Since liquid hydrazine at 40°C (104°F) exerts sufficient vapor pressure to support a 4.7 percent hydrazine-in-air mixture, it is possible for flammable mixtures to form at any temperature above 40°C. It is hypergolic with some oxidants such as hydrogen peroxide, fuming nitric acid, and nitrogen tetroxide. Water solutions at any concentration below 40 percent cannot be ignited.

10.2.3.2 Explosion Hazards

Hydrazine is an endothermic compound and may, therefore, be expected to undergo decomposition under appropriate conditions with the release of considerable energy. This property leads to hydrazine's usage as a monopropellant for rocket propulsion and power systems. The reaction of hydrazine catalyzed by metallic oxides may be violent and may cause an explosion or fire. Hydrazine is not sensitive to impact or friction but the vapors can be detonated by a spark; the vapor propogates detonation within the flammability limits. It is, therefore, not advisable to maintain a large quantity of vapor near or at the boiling point for any length of time.

10.2.4 Handling, Storage, and Distribution Requirements

Mild steel is incompatible with hydrazine because of the presence of oxides; only certain grades of stainless steel can be used. Conventional stainless steel fuel tank designs are quite adequate for unlimited service application. Pumps with stainless steel bodies and Teflon packing are suitable. Some aluminum alloys and titanium are also satisfactory.

Some oils used for lubrication are compatible with hydrazine. Special care must be taken in design of all flow systems to exclude stagnation zones in which heat may be present. Such zones may cause local decomposition of hydrazine and may lead to explosion.

Fuel transfer can be accomplished through stainless steel lines by low-pressure inert gas or by gravity feed. Plenty of water should be available to flush away any spillage.

Hydrazine should not be handled in facilities with wooden flooring, as spillage may cause the wood to ignite. Rags, paper, and other common organic materials should not be used around hydrazine since they may also ignite.

10.2.5 Critical Research Gaps

Since the freezing point of hydrazine is relatively high (34.5°F), it is not practical for use with automobiles operating in colder climates. Its freezing point may be lowered to a more suitable level by additives, but these additives should not change other properties of hydrazine. However, hydrazine is too toxic and dangerous to handle unless diluted with water. In this form it is ideal fuel for fuel cells but not for internal combustion engines. Experimental work is required to determine its suitability for use with the external combustion engine.

10.3 CURRENT STATUS

10.3.1 Production Rates

Both the Raschig and urea processes are used at present for the production of hydrazine.

Table 10-1 shows the producers of hydrazine and their production capacities.

10.3.2 Uses

Examples of the use of hydrazine and its derivatives follows:

- As a reducing agent for scavenging oxygen from boiler water to prevent corrosion of boilers
- As a reactive chemical in the reclaiming of platinum and copper catalyst

- As an unstable species, tetracene, an ignitor for explosives
- As physiologically active compounds for plant growth regulators, herbicides, and drugs
- As a source of energy in rocket propulsion.

The greatest consumption of hydrazine in the United States is for rocket fuel by the aerospace industry and related government facilities.

Table 10-1. Producers of Hydrazine (Ref. 10-1)

Country	Producer	Location	Process	Capacity,[a] million lb/year
United States	Olin Mathieson Chemical Corp.	Virginia[b]	Raschig	16
		Louisiana	Raschig	2
	Fairmount Chemical Co., Inc.	New Jersey	urea	0.6
		New Jersey	Raschig	1.5
	U.S. Rubber Co., Naugatuck Chemical Div.	Louisiana	Raschig	2
	National Polychemicals, Inc.	Massachusetts	urea	0.3
England	Whiffen & Sons, Ltd.[c]	Loughborough		2
		Widnes	Raschig	2
West Germany	Farbenfabriken Bayer, A.G.	Leverkusen	Raschig	4
France	Monopole des Poudres	Toulouse		0.6
	Société des Produits d'Azotes	Lannemezan		0.6
Spain	Química Sintética	Madrid		0.1
Japan	Hikari Chemical Industries Co., Ltd.	Ohmiya City		1
	Japan Hydrazine Co.	Tokyo		1
	Otsuka Chemical Co.	Osaka		2.5

[a] Based on anhydrous hydrazine.

[b] U.S. Government-owned plant, operated by Olin Mathieson Chemical Corp.

[c] A division of Fisons, Ltd.

10.3.3 Consumer Cost

Anhydrous hydrazine is now being delivered to the U.S. Air Force under contract at a cost of $1.23/lb. It is anticipated that the cost of hydrazine may be lowered to $0.75/lb. in large tonnage production (Ref. 10-2). These costs are an order of magnitude higher than those for gasoline-powered automobiles when compared on a utilization per mile basis.

10.4 PROJECTED STATUS

The projected availability of hydrazine is dependent upon availability of the raw materials for its manufacture. In this case, the basic raw material is hydrogen, which is used to produce ammonia, which is then synthesized to hydrazine.

Hydrogen production from natural gas feedstock appears in short supply in the years ahead. Alternative hydrocarbon supply sources, such as propane and butane, also appear limited.

Hydrogen production from coal is technically feasible but not economically attractive compared to SNG or liquid hydrocarbon fuels from coal. Water electrolysis offers the most promise as a source of large-scale hydrogen production. However, problems with supplying adequate electrical power are involved in such an approach (see Section 9.4.1.2).

Capital costs for hydrazine production facilities would certainly be more than for hydrogen or ammonia plants, since these liquids are merely feedstocks for the formulation of hydrazine.

The hazards to health and safety may be a factor that could inhibit the use of hydrazine as an automotive fuel. The cost of producing hydrazine, which is an additive to the cost of producing its raw materials, is another deterrent.

The many deficiencies of hydrazine fuel in application to automobile heat engines lead to the conclusion that it is unsuitable as an alternative to petroleum-based fuels, particularly for near-term use.

11. FUELS REFORMED ON-BOARD THE VEHICLE

Operation of gasoline-fueled spark ignition internal combustion engines at lean air-fuel ratios [i.e., air-fuel ratios greater than stoichiometric (or 15:1)] can result in the reduction of exhaust emissions without the addition of emission control devices, as illustrated in Figure 11-1. As can be noted from the figure, at the stoichiometric air-fuel ratio, NO_x production is very high while HC and CO production is relatively low. For air-fuel ratios between approximately 17 and 19, levels for all three constituents are reduced considerably from peak values. Currently, gasoline engines are normally operated as air-fuel ratios below approximately 17 to avoid rough engine operation which occurs as the lean limit of gasoline-air combustion is approached. This inherent lean limit then prevents the achievement of lowered NO_x emissions which occur at still leaner mixtures.

One approach that is being investigated as a means of extending the lean operating limits of gasoline engines for the control of NO_x is the incorporation of a fuel-reformer unit between the gasoline tank and the carburetor of the gasoline engine-powered conventional automobile. The fuel reformer device is a unit that converts all or a portion of the engine's fuel requirements from gasoline (or other liquid hydrocarbon fuel) to a gaseous product prior to induction into the engine. This gaseous reformed fuel is principally hydrogen and carbon monoxide. The hydrogen, with its wide flammability limits, enables operation of the engine at much leaner mixtures than are obtainable with gasoline only.

Another attribute of lean operation is an increase in engine thermal efficiency resulting from inherent characteristics of the thermodynamics of the air cycle. Unless other system inefficiencies (e.g., fuel reformer losses) or deleterious effects are introduced, increased thermal efficiency should result in improved vehicle fuel economy (miles per gallon).

There are, however, several disadvantageous consequences to lean operation. Chief among these is the reduced specific power output of

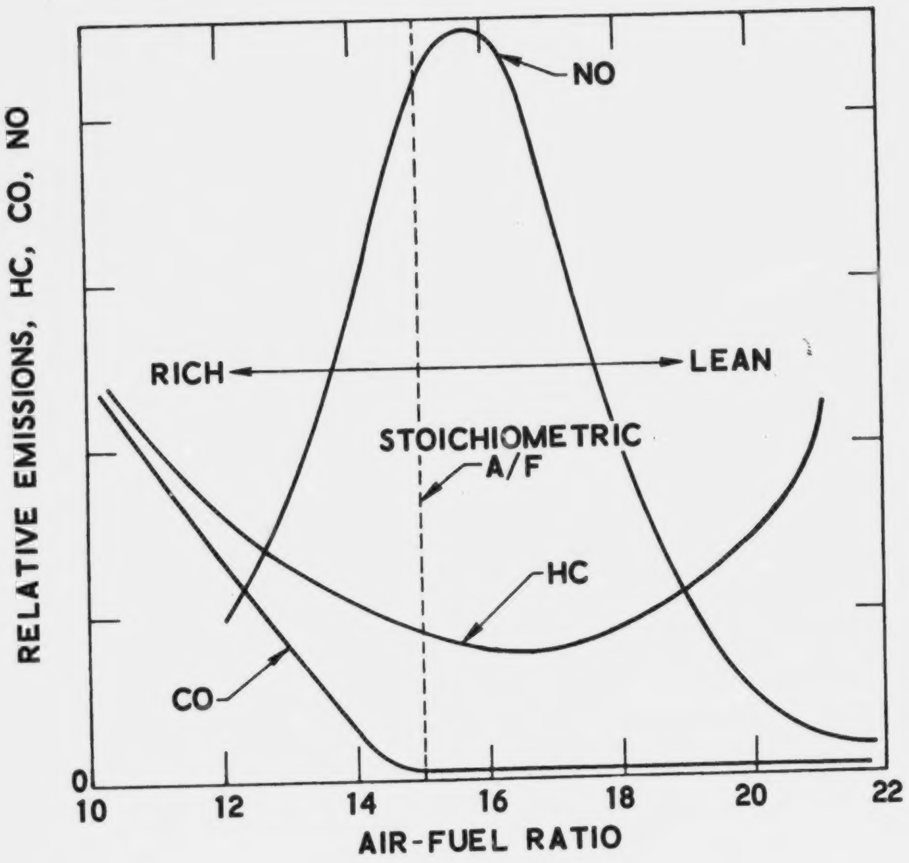


Figure 11-1. Effect of Air-Fuel Ratio on Emission Levels (Gasoline Spark Ignition Engine)

the engine, which would necessitate the use of a larger-displacement engine for the same maximum power output. Also, in the case where a reformer is used to facilitate lean operation, the reformer products, being gaseous in nature and at elevated temperature, can reduce engine volumetric efficiency and still further reduce specific power output. Another deleterious effect, as can be noted from Figure 11-1, is that HC emissions rise as air-fuel ratio is increased to reduce NO_x emissions.

Thus, the potential for achieving reduced NO_x emissions and improved fuel economy must be balanced against reduced specific power output, possible HC increases, and increased system configurational and operational complexities when evaluating the relative merit of concepts for reforming fuel on-board the vehicle to permit lean operation.

The following sections discuss and summarize the characteristics of a number of specific fuel reformer devices and the available data concerning emissions, fuel economy, and other system operational features. Also included are the results of recent General Motors tests with hydrogen-supplemented gasoline fuel. These tests simulate to a first order engine operation with reformer products and are, therefore, included to summarize data relevant to the reformed fuel concept.

Although this volume of the report is principally directed to alternative fuels, the interrelationship of the fuel reformer and the engine makes it necessary to discuss engine-related items and characteristics in order to adequately treat the reformed fuel concept.

11.1 CHARACTERIZATION

11.1.1 Fuel Type

Fuels reformed on-board vehicles are gaseous fuels resulting from thermal decomposition or catalytic cracking of liquid hydrocarbon fuel stored on-board the vehicle in a conventional manner, i.e., in the normal gasoline tank. These gaseous reformed fuels result from the passage of the stored liquid hydrocarbon fuel through a fuel reformer device (or gas generator) just prior to the introduction of the reformed fuel into the air induction and mixing system of the heat engine. The principal constituents of the gaseous reformed fuel are hydrogen (H_2) and carbon monoxide (CO), although water vapor, carbon dioxide (CO_2), nitrogen (N_2), methane (CH_4), and other hydrocarbons may also be present, depending upon the specific reformer device used and its principle of operation (discussed further in Section 11.1.3).

11.1.2 Reserves or Raw Material Sources

In general, reformed fuels may be processed from a variety of liquid hydrocarbon fuels including: gasoline, kerosene, jet fuel, diesel fuel, home heating oil, heptane, hexane, LPG, etc. Specific reformer devices or systems, however, may be designed to operate on a single grade of hydrocarbon fuel or in a more limited range of hydrocarbon fuel choices.

Thus, reformed fuels are in turn limited by the reserves and/or raw material sources for conventional petroleum or nonpetroleum hydrocarbon liquids as set forth previously in Sections 3, 4, and 7.

11.1.3 Methods of Manufacture (Fuel Reformer Concepts)

All of the variously proposed hydrocarbon fuel reformers (or gas generators) for mobile vehicle use have their roots in stationary petroleum gasification processes developed for production of hydrogen by steam reformation, principally the partial oxidation and the catalytic reformation processes. Versions of partial oxidation gasification have been developed principally by Texaco, Shell, Exxon, and Lurgi. Catalytic reformation processing has been developed by M. W. Kellogg, Foster-Wheeler, Mobil, Exxon, and many others.

Hydrogen is produced by steam reformation of gasoline according to well-known refinery technology and the following ideal summary reaction equation (for isooctane) (Ref. 11-1):

$$C_8H_{18} + 8H_20 \rightarrow 8CO + 17H_2 \qquad (11\text{-}1)$$

In the non-ideal case, however, lower reformation conversion efficiencies and the specifics of the particular process used introduce other process products. To illustrate one such effect, consider the conversion of isooctane at 1450°R. At 1450°R the equilibrium conversion of the hydrocarbon to reformer products is about 70 percent. The steam reforming action in this case would be (Ref. 11-2):

$$C_8H_{18} + 8H_20 \rightarrow 5.6CO + 11.9H_2 + 0.3C_8H_{18} + 2.4H_20 \tag{11-2}$$

thus reducing CO and H_2 quantities in the product gases and introducing steam and residual hydrocarbons.

Further, partial oxidation systems consume oxygen, either as a pure gas or from air, to provide the endothermic heat (via combustion) for gasification. In this process, part of the fuel feedstock is combusted with the oxygen or air within the reformation chamber. The alternative use of air for combustion in these processes produces a yield gas heavily diluted by nitrogen. Also, stationary installations incorporating partial oxidation processes fail to gasify the feedstock completely, producing an effluent by-product of aromatics, tars, and coke or soot.

Catalytic steam reformation has been successfully applied to methane, propane, condensate,and naphtha, yielding a high quality synthesis gas mixture containing 60 percent hydrogen or more (by volume). Such processing involves a steam-hydrocarbon reaction within a heated process tube which is packed with a granular catalytic bed to promote the reaction. The heat is supplied by heat exchange with an external heat source, thus no air or oxygen is required for combustion in the process chamber, as is required in the partial oxidation process. Since no air is used in the process, the yield gas is not diluted with nitrogen. This process has a high thermal efficiency in conversion (typically 85 to 95 percent as compared to 67 percent for stationary partial oxidation installations) and does not have soot and tars in its gas product.

For mobile vehicle use, a number of different hydrogen gas generator (or fuel reformer) concepts have been proposed. Those concepts sufficiently disclosed are separately discussed in the following sections. Their developmental activities are exploratory in nature and none has yet resulted in on-the-road vehicle tests with an on-board fuel reformer.

11.1.3.1 International Materials Corporation Concept

In 1971 the International Materials Corporation disclosed by patent (Ref. 11-3) and SAE paper (Ref. 11-4) the principles of an on-board hydrogen gas generating system. Briefly, it is a system which mixes a liquid hydrocarbon fuel with water and heats the mixture sufficiently to cause thermal decomposition resulting in hydrogen gas which is fed to an internal combustion engine. Water from the engine exhaust is recycled for mixing with the hydrocarbon fuel. To date, effort has been limited to exploratory development of the reformer unit only. The following description of the system and its operation is abstracted from Reference 11-4.

11.1.3.1.1 Brief Description of the Reformed Fuel System*

Water is condensed from the engine exhaust by muffler heat exchangers; this water, as shown in Figure 11-3 and 11-4 is pumped in excess of the chosen system pressure of approximately 800 psi through a metering orifice to a vaporization chamber. The steam is then led through an initial length of coil to provide superheating to near 1,000°C, at which point gasoline is injected through a metering orifice at the same pressure. The length of the lead-in tubing is sufficient to vaporize the gasoline, with its lower specific heat. In the next downstream region of coil reactions, the primary production of CO and H_2 is completed. A second injection of low-temperature steam follows for a quenching effect, and the CO shift occurs in the low-temperature region. The product gases are then led from the canister, through suitable

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*Component location is shown in Fig. 11-2.

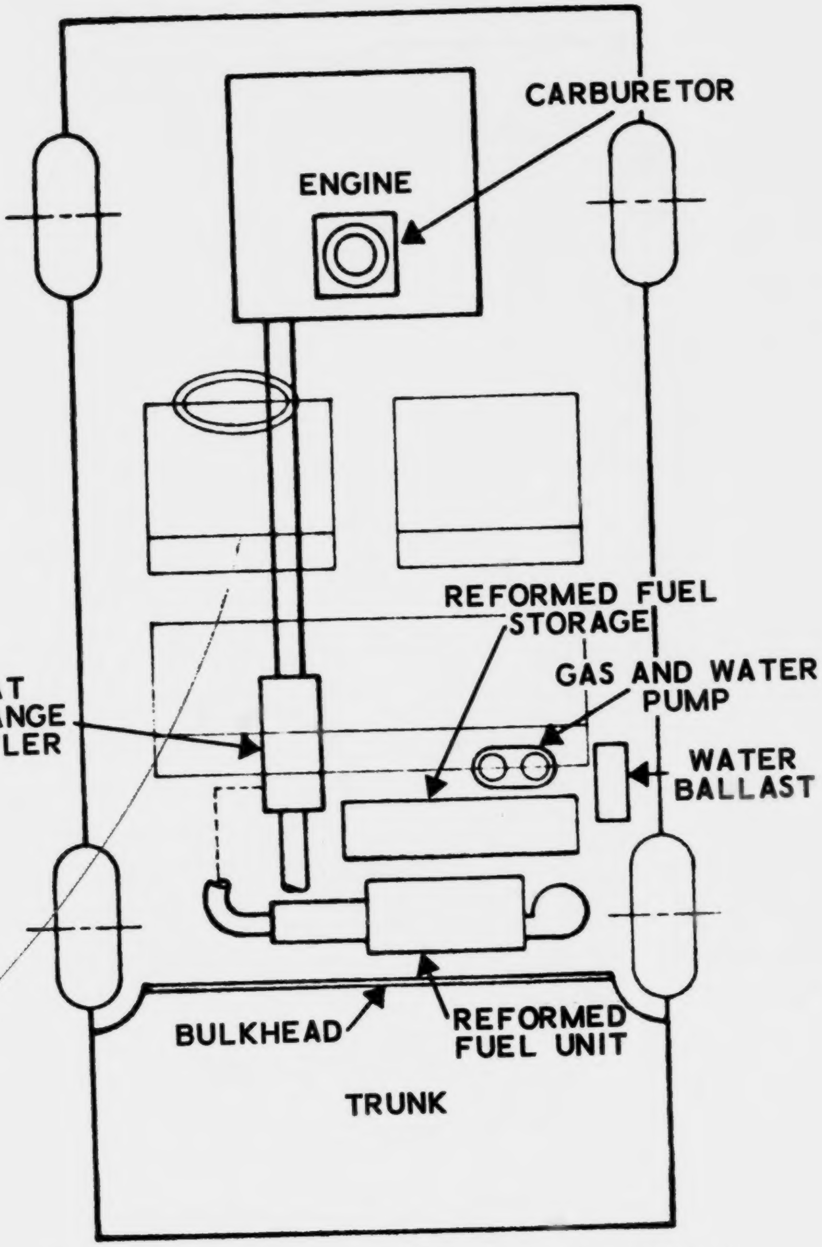
CARBURETOR
ENGINE
REFORMED FUEL STORAGE
GAS AND WATER PUMP
HEAT EXCHANGE MUFFLER
WATER BALLAST
BULKHEAD
REFORMED FUEL UNIT
TRUNK

Figure 11-2. Component Location, International Materials Concept (Ref. 11-4)

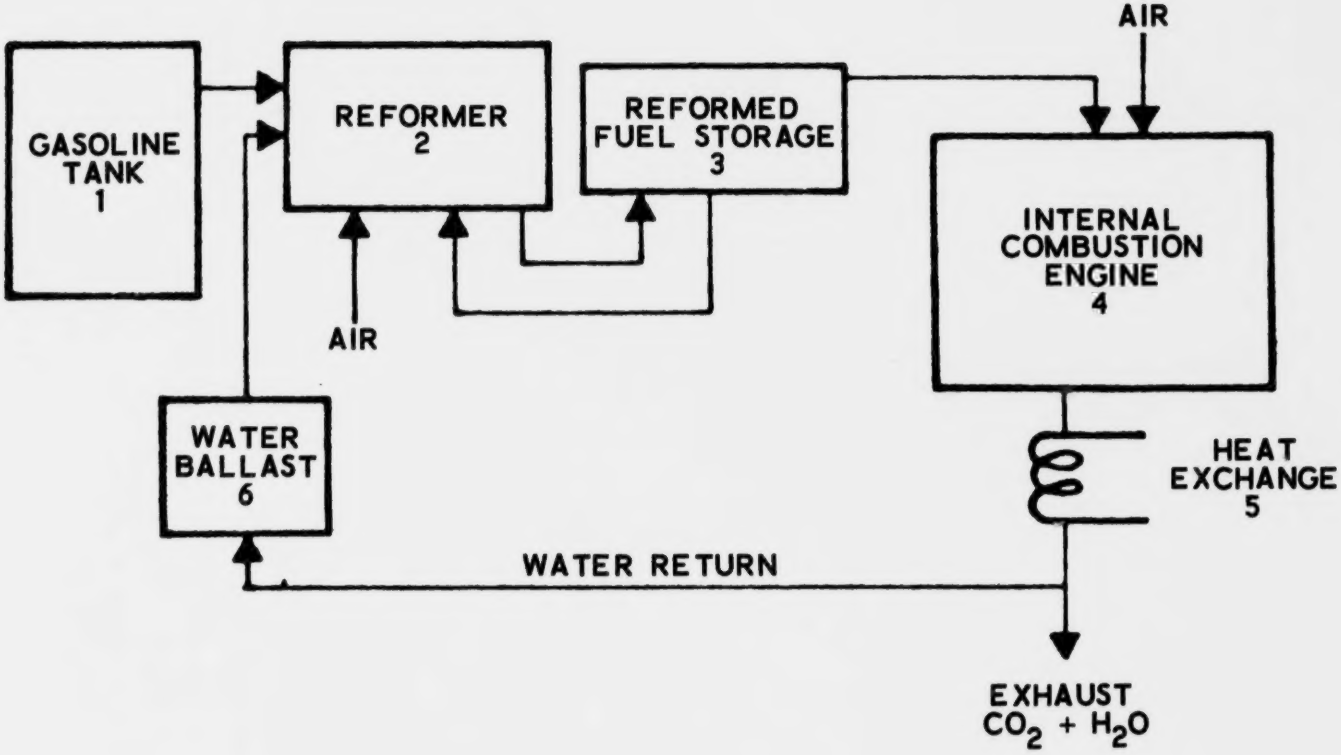
GASOLINE TANK 1
REFORMER 2
REFORMED FUEL STORAGE 3
AIR
AIR
INTERNAL COMBUSTION ENGINE 4
HEAT EXCHANGE 5
WATER BALLAST 6
WATER RETURN
EXHAUST $CO_2 + H_2O$

Figure 11-3. Block Diagram, International Materials Concept (Ref. 11-4)

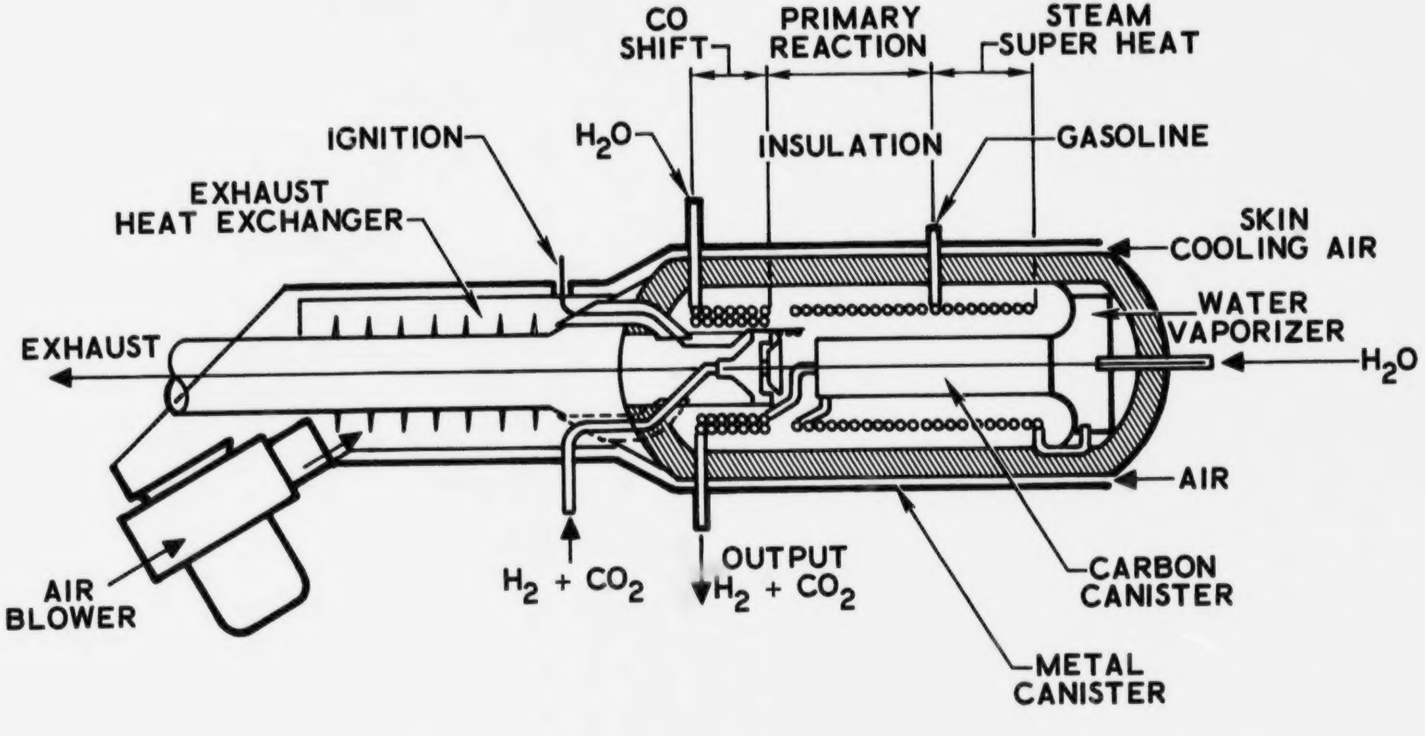
CO SHIFT
PRIMARY REACTION
STEAM SUPER HEAT
IGNITION
H_2O
INSULATION
GASOLINE
EXHAUST HEAT EXCHANGER
SKIN COOLING AIR
WATER VAPORIZER
EXHAUST
H_2O
AIR
AIR BLOWER
$H_2 + CO_2$
OUTPUT $H_2 + CO_2$
CARBON CANISTER
METAL CANISTER

Figure 11-4. Reformer Canister Cross Section, International Materials Concept (Ref. 11-4)

heat recovering structures. The reformed fuel is then directed to a small storage tank that services the engine. This tank is the source of reformed fuel when the engine is started with the reformer cold. A pressure switch detects depletion of tank pressure, causing the reformer to begin replenishing the tank. This fuel storage also serves as the source of combustion energy for the reformation process. Theoretical efficiencies of the reformer are approximately 59.7 percent without heat exchange. Efficient heat exchange (that is, exhaust temperature below 260°C) indicate efficiencies in the range of 86 to 87 percent.

11.1.3.2 Phillips Petroleum Company Concept

In 1973 the Phillips Petroleum Company (Ref. 11-2) disclosed by patent (as assignee) a method and apparatus for passing exhaust gases from an engine through a fuel regenerator in indirect heat exchange with fuel and steam in contact with a catalytic bed for steam reforming the fuel. The system is illustrated in Figure 11-5, and the following description of system operation is abstracted from Ref. 11-2.

11.1.3.2.1 Operational Features

In this concept, a hydrocarbon liquid fuel such as diesel fuel, gasoline, jet fuel, kerosene, or liquefied petroleum gas is initially delivered from the fuel reservoir to the fuel injector for injection into the engine. The engine is operated until the temperature of the exhaust from the combustion chamber of the engine increases to a sufficient level.

Fuel and water are then metered into the inner chamber of the fuel regenerator tube (by proportioning pumps) and contacted with the catalyst bed of the inner chamber in indirect heat exchange with exhaust gases discharging from the engine and passing through the outer chamber of the fuel regenerator tube. Ordinarily, a ratio of water to hydrocarbon weight of about 1.2 or higher is satisfactory. The pressure within the inner chamber of the fuel regenerator is maintained at a preselected pressure during injection of fuel and water by a pressure regulator.

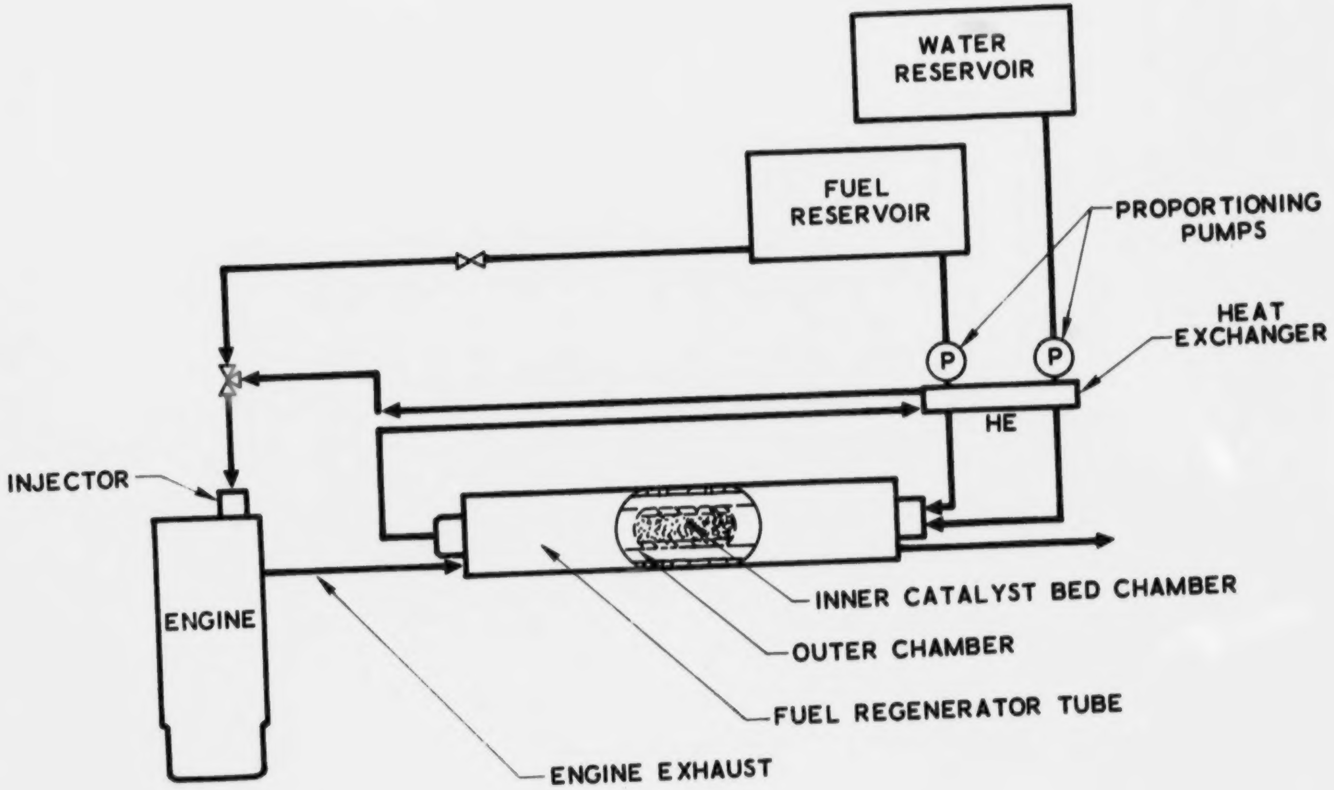
WATER RESERVOIR
FUEL RESERVOIR
PROPORTIONING PUMPS
HEAT EXCHANGER
P
P
HE
INJECTOR
ENGINE
INNER CATALYST BED CHAMBER
OUTER CHAMBER
FUEL REGENERATOR TUBE
ENGINE EXHAUST

Figure 11-5. Fuel Reformer Concept, Phillips Petroleum Company (from Ref. 11-2)

The fuel and water mixture is maintained in contact with the catalytic bed until the mixture is heated to a temperature sufficient for reforming the fuel mixture in the presence of the catalyst and producing a gaseous fuel. The gaseous fuel is delivered to the engines fuel injector and mixed with air; the resultant mixture is injected into the engine and combusted.

The temperature of the exhaust gases passing through the fuel regenerator adjacent the catalytic bed should be at least 950°F before the fuel and water is injected into the catalyst bed.

To reduce the pollutants discharging from the engine during operation thereof, the reformed fuel should be produced at a rate such that delivery of the reformed fuel to the engine is sufficient to operate the engine at the desired speed and load, and delivery of the liquid fuel to the engine can be terminated.

11.1.3.3 Jet Propulsion Laboratory Concept

In October, 1973, the Jet Propulsion Laboratory (JPL) of the California Institute of Technology disclosed a concept for improving the emissions and fuel economy of conventional spark ignition engines (Ref. 11-1).

Basically, the concept is to blend small amounts of hydrogen with gasoline in a carburetor to allow combustion to proceed at ultra-lean conditions. As shown in Figure 11-6 a gaseous mixture (largely hydrogen) is generated on-board the vehicle by feeding gasoline and air* to a hydrogen generator. The generated gas is mixed with gasoline and fed to a conventional engine. The required hydrogen is produced in the generator, and no hydrogen is stored on-board the vehicle.

The most critical element in development of this system is the hydrogen generator. The design chosen is similar to that used for commercial

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*Previously water was also fed to the hydrogen generator, but recent generator developments allow elimination of the water feed (Ref. 11-5).

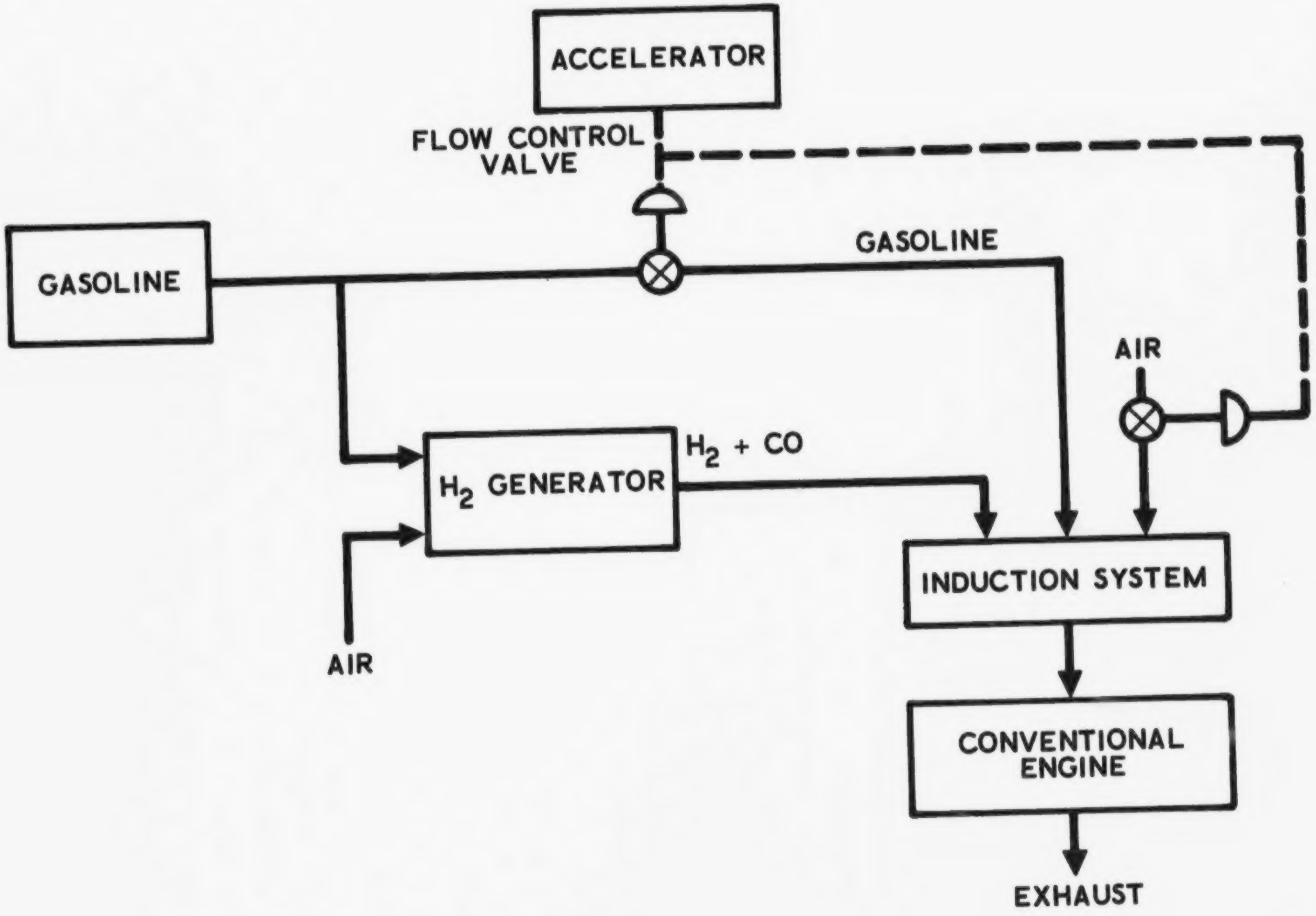

ACCELERATOR
FLOW CONTROL VALVE
GASOLINE
GASOLINE
AIR
H_2 + CO
H_2 GENERATOR
AIR
INDUCTION SYSTEM
CONVENTIONAL ENGINE
EXHAUST

Figure 11-6. JPL System (Ref. 11-5)

production of hydrogen from hydrocarbons. (The process is called partial oxidation fuel reforming.) In this process gasoline, water, and air are reacted at 1500 to 2000°F, forming a gaseous mixture composed of hydrogen, carbon monoxide, plus various hydrocarbons and diluents. Heat is supplied by pumping air into the generator and burning a portion of the gasoline. The reaction takes place in a reactor with or without the use of catalysts. The maximum theoretical hydrogen yield for a hydrogen generator with water, gasoline, and air feed is 29 percent by volume. When no water feed is used the generator air-fuel mass ratio must be greater than five to avoid soot formation. Under these conditions the maximum theoretical hydrogen yield is 25 percent by volume. A current JPL catalytic generator (Figure 11-7) yields 22 percent hydrogen by volume with a small trace of soot. This operation is achieved with gasoline and air feed only and no water is used. The catalytic generator has an efficiency of 81 percent. This is a major improvement over an earlier JPL generator which produced 14.5 percent by volume hydrogen with an efficiency of 67 percent and which required water feed. Development is continuing toward eliminating the need for catalysts in the hydrogen generator (Ref. 11-5).

11.1.3.4 Siemens Catalytic Carburetor Concept

The general features of a catalytic carburetor system under development by the German industrial firm, Siemens, was disclosed in December 1973 (Ref. 11-6) from which the following descriptive material was abstracted.

Although termed a catalytic carburetor, it is a gas generator that breaks up the gasoline molecules into gaseous components such as hydrogen, carbon monoxide, and methane before the fuel is mixed with air. Some air is necessary for the gasification process, but the ratio is 1 part air, by weight, to 20 parts gasoline.

As shown in Figure 11-8, fuel is metered by electromagnetically controlled injectors and enters from both sides at the top of an enclosure about the carburetor. A priming device feeds in small amounts of air mixed with recirculating exhaust gas. The fuel enters the catalyst bed and is gasified in a cracking process. The purpose for recirculating the exhaust

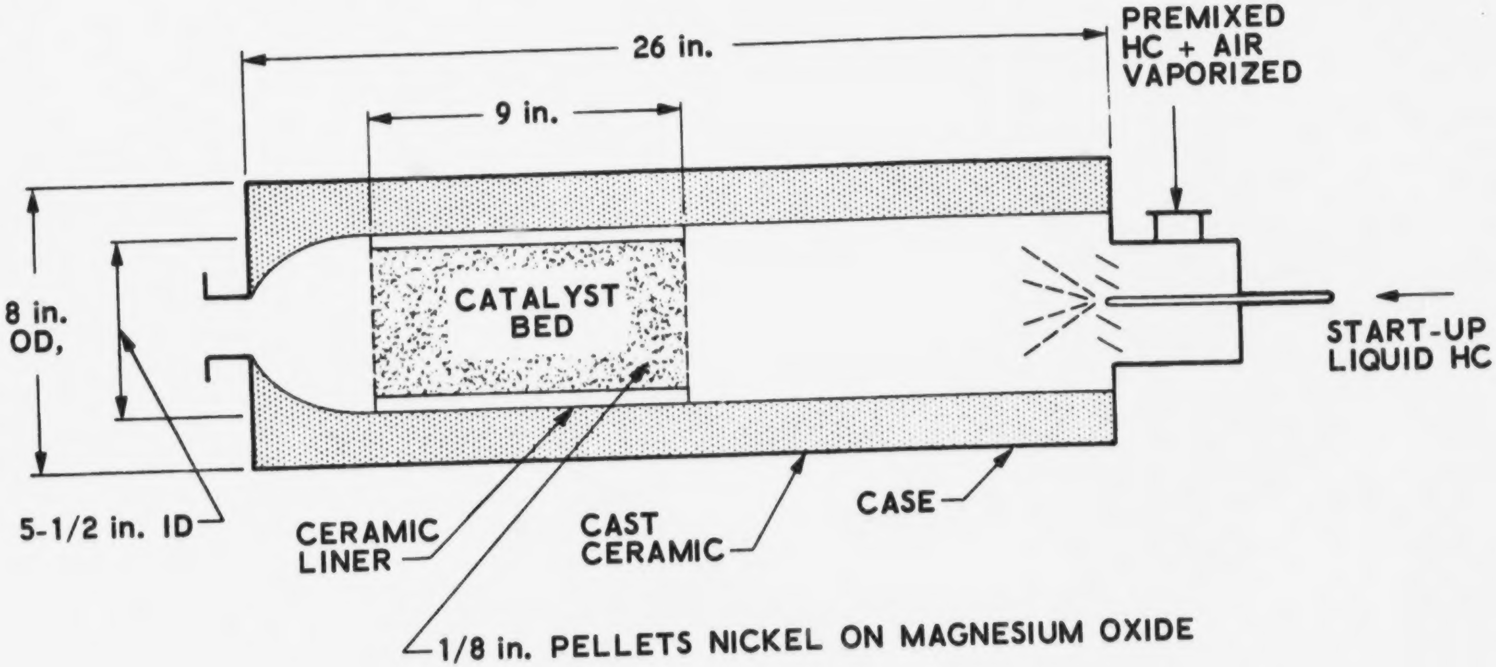
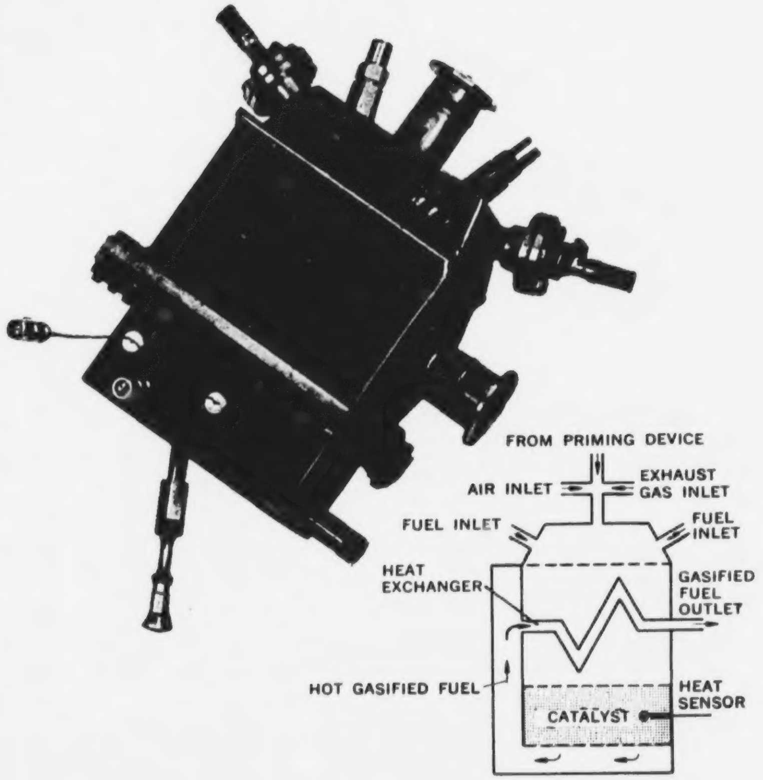

26 in.
PREMIXED
HC + AIR
VAPORIZED
9 in.
8 in.
OD,
CATALYST
BED
START-UP
LIQUID HC
5-1/2 in. ID
CERAMIC
LINER
CAST
CERAMIC
CASE
1/8 in. PELLETS NICKEL ON MAGNESIUM OXIDE

Figure 11-7. Catalytic Hydrogen Generator (JPL; Ref. 11-5)


FROM PRIMING DEVICE
AIR INLET
EXHAUST GAS INLET
FUEL INLET
FUEL INLET
HEAT EXCHANGER
GASIFIED FUEL OUTLET
HOT GASIFIED FUEL
HEAT SENSOR
CATALYST

A small box about 12 inches high encloses the carburetor unit. The diagram at right shows the flow path of the gaseous fuel from the catalyst bed through the built-in heat exchanger. Fuel is metered by electronic computer.

All functions in the Siemens fuel system are controlled by an electronic unit. Fuel is gasified before being mixed with air into a combustible charge. It's all gas, without fuel droplets, so mixture can be extremely lean. That means complete combustion and more mpg.

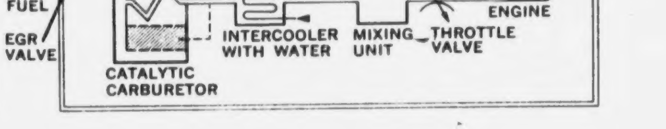

METERING VALVE
ELEC-TRONIC CONTROL UNIT
FUEL
AIR
AIR VALVES
AIR
AIR CLEANER WITH THERMISTOR
AIR VALVE
M
PRIMING DEVICE
HEAT SENSOR
M
M
FUEL
EGR VALVE
CATALYTIC CARBURETOR
INTERCOOLER WITH WATER
MIXING UNIT
THROTTLE VALVE
ENGINE

Figure 11-8. Features of Siemens Catalytic Carburetor System (Ref. 11-6)

is to heat up the catalyst. It will not work below a certain temperature. Siemens engineers won't identify the catalyst but claim it does not contain noble metals.

The gas is formed at an elevated temperature and must be cooled before it can be mixed with air. The cooling takes place in two stages. First, the gas flows through a heat exchanger contained within the carburetor body. Some heat is recovered and goes back to the catalytic bed. Then the gas flows through a water-cooled radiator before being led to the mixing unit.

The air-fuel charge is created in the mixing unit, when the gasified fuel is metered into fresh air that has entered the plenum chamber mounted upstream from the mixing unit and intake manifold. The air-fuel ratio is closely controlled by an electronic control unit (computer).

This small computer also controls the priming device and the quantity of raw fuel admitted to the catalytic carburetor. The computer is wired to sensors for engine speed and load, ambient temperature, and air density; it automatically adjusts fuel quantity and air-fuel ratios as incoming information is received. Adjustments are made in milliseconds.

Despite intercooling, the air-fuel mixture still has a higher-than-ambient temperature when it enters the combustion chambers. This brings with it the disadvantage of reduced cylinder filling. Siemens engineers estimate that the catalytic carburetor gives volumetric efficiency between 10 and 20 percent lower than conventional carburetors.

However, this loss can be restored by raising the compression ratio. The catalytically cracked fuel offers high knock resistance (high octane number) and is compatible with high-compression engines. The raw gasoline must be lead-free, as lead will contaminate the catalyst.

11.1.4 Physical and Chemical Properties

As noted previously, ideal steam reformation of hydrocarbon fuels would yield only H_2 and CO as the reformer fuel products. However, process inefficiencies and the differences in reformer design approach and process characteristics combine to produce reformed fuels with a variety of other constituents.

In the case of the partial oxidation process approach, results from the JPL concept program can be used to illustrate these effects (Ref. 11-5). The reformed fuel products, or the output composition of the partial oxidation process hydrogen generator, are illustrated in Table 11-1 for both the theoretical case and the experimental catalytic laboratory generator. As can be noted, even in the ideal case, in addition to the desired H_2 and CO there is a substantial amount of nitrogen generated (from the air used to provide process combustion heat), as well as carbon dioxide, methane, and steam. In the actual case shown, the steam content is reduced and there are other hydrocarbon species present.

Table 11-1. Catalytic Hydrogen Generator Output Composition (JPL, Ref. 11-5)

Component	Volume %	
	Theoretical	Actual
H_2	24.3	21.60
CH_4	0.1	1.54
C_2H_4	--	0.85
CO	21.9	23.20
CO_2	1.4	1.16
H_2O	2.0	1.30
N_2	50.3	50.35
	100.0	100.00
Feed: Indolene and air Trace quantities of soot		

In the case of a catalytic-steam reformation process, Reference 11-2 indicated reformer products with the following composition, in mol percent:

Methane	35.3
Hydrogen	30.0
Carbon monoxide	3.3
Carbon dioxide	16.4
Water	15.0

The above composition was expressed as typical of an equilibrium product of steam reacted with hexane at 1,000 °F and using a steam-hexane ratio of 1.71 pounds per pound with a water condenser operating at 180°F to condense out a portion of the water content of the effluent.

A complete description of the reformed fuel products from the Siemens "catalytic carburetor" is not available; however, they do mention that methane is present as well as hydrogen and carbon monoxide. Since some air is used in their device (one part air, by weight, to 20 parts of gasoline), some nitrogen generation would also be expected.

A complete delineation of the reformed fuel products from the International Materials Corporation concept (Ref. 11-4) is not currently available in the literature. Reference 11-7 indicates that the products include H_2, CO, CO_2, and CH_4.

11.1.5 Combustion Characteristics

Although specific combustion characteristics of reformed fuel products have not yet been detailed, it would be expected that effects of the hydrogen gas present would predominate and that the excellent combustion characteristics of hydrogen (see Section 8) would similarly apply to the hydrogen-gas generator products, unless excessive amounts of diluents (steam, nitrogen) were present. Laboratory tests of a V-8 engine with products from an experimental generator were conducted by JPL (Ref. 11-1), and engine operation was generally similar to that obtained with mixtures of gasoline and pure hydrogen (Ref. 11-8).

11.2 SUITABILITY FOR USE AS AN ENGINE FUEL

11.2.1 Engine/Vehicle Compatibility

Since the principal combustible constituent of reformed fuels is hydrogen, they should be very compatible with engine combustion requirements, as delineated previously for hydrogen in Section 8.1.5 . In addition, on-board fuel reformation provides conventional storage of the basic liquid hydrocarbon fuel, much the same as gasoline is stored on-board today's automobiles, thus negating the well-known storage problems attendant to gaseous and liquid hydrogen fuels (Section 8.2.6).

There are, however, ancillary effects caused by the method of reformer operation and the characteristics of the reformed fuel in terms of its gaseous nature, its temperature at inlet to the engine, and its species composition. These effects are discussed in the following sections.

11.2.1.1 Method of Reformer Utilization

Fuel reformers may be utilized to process the entire engine fuel requirements or to gasify only a portion of the engine fuel requirements (i.e., engine operates on liquid gasoline plus reformer gaseous products). In either case, partial or total fuel reformation, the principal objective to date has been to operate the engine at lean air-fuel mixtures in order to reduce the amounts of HC, CO, and NO_x exhaust emissions (Refs. 11-1, 11-2, 11-4, and 11-6) as discussed more fully in Section 11.2.3.

The gaseous hydrogen in the reformed fuel, with its high flame velocity and ready combustibility over a wide range of air-hydrogen mixtures, enables operation at fuel-air ratios much leaner than possible with gasoline. This is illustrated for hydrogen-plus-gasoline mixtures in Figure 11-9 from General Motors tests (Ref. 11-9) with a single-cylinder engine. Shown is the lean limit equivalence ratio* as a function of the amount of gaseous hydrogen present in the hydrogen plus gasoline mixture. The lean

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* equivalence ratio $= \frac{\text{(actual fuel air ratio)}}{\text{(stoichiometric fuel air ratio)}} = \phi$

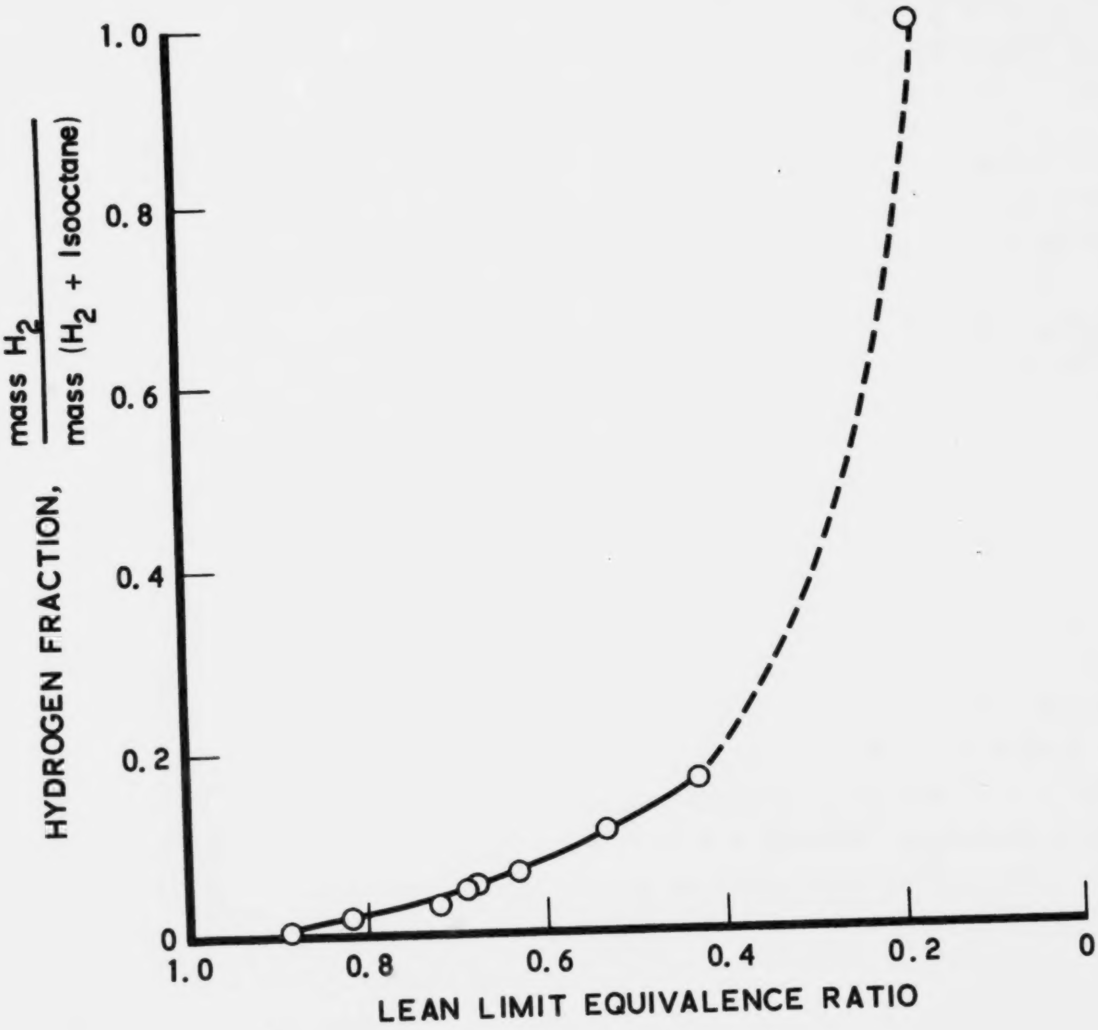

Figure 11-9. Effect of Hydrogen Addition on Lean Operating Limit with Isooctane as the Base Fuel (Ref. 11-9)

operating limit for pure isooctane (0.89 equivalence ratio) could be extended to an equivalence ratio of 0.55 with a hydrogen fraction of 0.10 and to an equivalence ratio of 0.40 with a hydrogen fraction of 0.20.

11.2.1.2 Effects on Power Output

A concomitant effect of very lean operation is a loss in engine power output, whether the fuel be conventional gasoline, gaseous reformed fuel products, or mixtures thereof. Figure 11-10 illustrates results obtained by General Motors with hydrogen-plus-gasoline mixtures in a single-cylinder engine. The indicated horsepower decreased about 40 percent for the change in mixture ratio from $\phi = 1.0$ to $\phi = 0.55$ due to the reduced energy input at the leaner mixture.

In addition to the power loss occasioned by lean operation, further power losses with reformed fuels may be caused by decreased volumetric efficiency and fuel dilution effects. The volumetric efficiency is reduced due both to the gaseous nature of the reformed fuel and the higher temperatures of the reformed fuel products entering the engine. Although the specific fuel reformed concept usually provides for cooling the gas-generator products prior to induction by the engine, the resultant cooled gaseous reformed fuel product may be several hundred degrees hotter than normal inlet air and fuel temperatures.

As noted in Section 11.1.4, the reformed fuel has, in addition to hydrogen, some amounts of carbon monoxide, methane, water, unreacted hydrocarbons, and, in the case of partial oxidation processes, large fractions of nitrogen from the air used in the combustion process. While the diluents' steam and nitrogen might be expected to have salutory NO_x emission reduction effects, they also reduce specific power output if quantities are too large.

Table 11-2 illustrates the effects on engine power of gaseous fuel dilution, lean operation, and reformer products for the case of a JPL partial oxidation experimental fuel reformer operated in laboratory tests with a 350-CID V-8 engine. As shown, the effect of gaseous hydrogen in a gasoline-plus-hydrogen fuel mixture reduces engine horsepower (at 2,000 rpm)

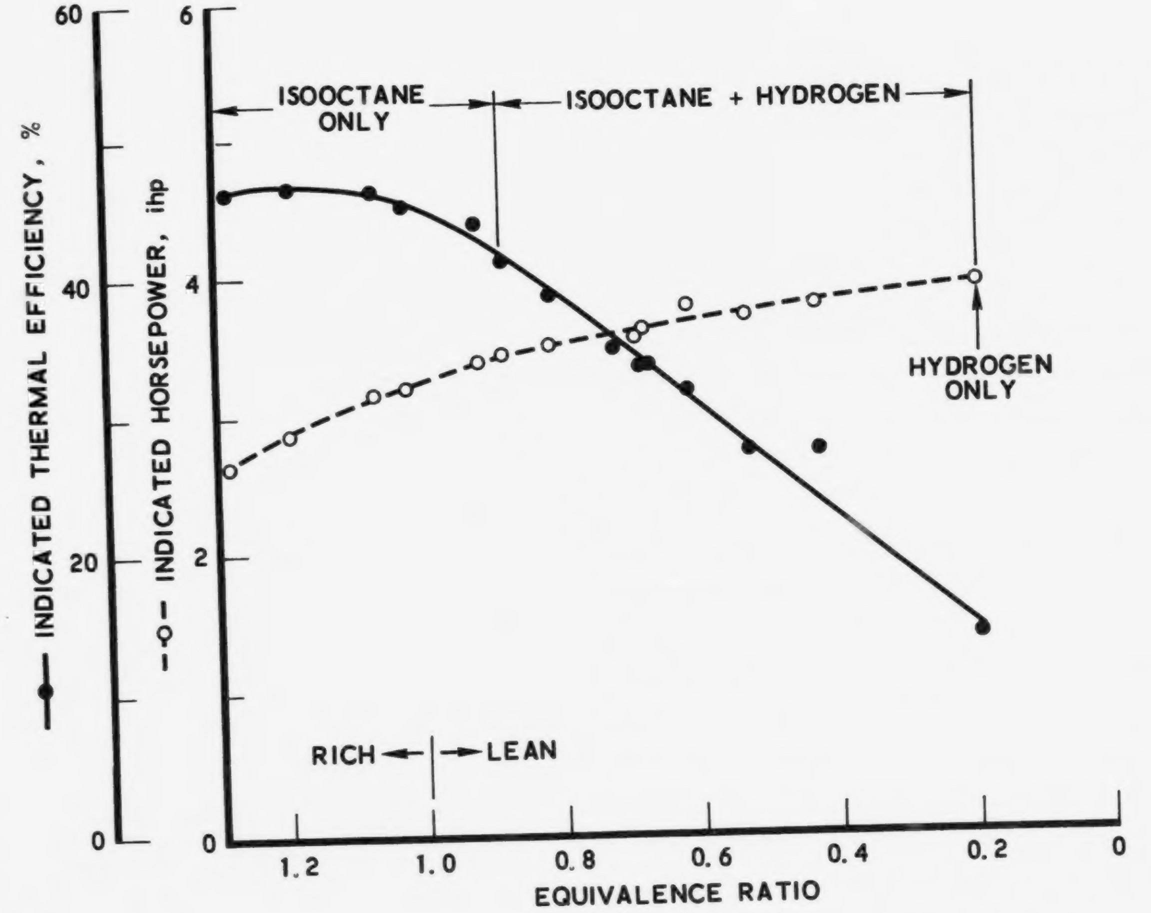

Figure 11-10. Effect of Ultralean Operation on Engine Power and Efficiency with Hydrogen-Supplemented Fuel (Ref. 11-9)

Table 11-2. Summary of Operational Characteristics, JPL System (Ref. 11-1)

Engine Maximum Indicated H. P. at 2000 rpm Condition	Current Engine and H_2 Gen.
Gasoline $\phi = 1.0$	91
H_2 + Gasoline $\phi = 1.0$	88
H_2 + Gasoline $\phi = 0.6$	61
H_2 Generator + Gasoline $\phi = 1.0$	75
H_2 Generator + Gasoline $\phi = 0.6$	54

from 91 to 88. With this same fuel mixture, reducing the equivalence ratio from stoichiometric ($\phi = 1.0$) to lean operation ($\phi = 0.6$) further reduces the power output to 61 horsepower. With reformer products instead of the hydrogen, at $\phi = 1$ the power is reduced from 88 to 75 and at $\phi = 0.6$ the power is reduced from 61 to 54.

Siemens (Ref. 11-6) reports that their "catalytic carburetor" produced no power loss (over the standard carburetor) when operated at $\phi = 0.8$ in a small (122-cubic inch) engine, and it produced a 4.14 percent gain in power at stoichiometric conditions ($\phi = 1.0$). However, at leaner conditions ($\phi = 0.70$ to 0.75) there was a sizeable power loss (15 to 25 percent).

It should be noted that the aforementioned power losses apply only in the case where the fuel reformer is operating. Some concepts provide for the capability to bypass the reformer under certain operating conditions (e.g., high-speed highway operation). By operating an engine with gasoline only, full engine power would be available at normal engine efficiency.

11.2.2 Fuel Economy Effects

Improved fuel economy for vehicles operated with reformed fuels has been postulated to result from (1) higher engine thermal efficiencies as a result of lean operation and (2) reduced throttling losses at part-load conditions by using fuel throttling control instead of air or intake charge throttling; this latter approach is rendered feasible because of the combustibility of hydrogen-air mixtures over the wide range of air-fuel ratios that would be encountered during unthrottled part load engine operation.

Engine-indicated thermal efficiencies were measured by General Motors (Ref. 11-9) for a single-cylinder engine operating on hydrocarbon-supplemented gasoline, as shown in Figure 11-10. As can be noted, the indicated thermal efficiency increased from 33 percent for an equivalence ratio of 1.0 to about 37 percent at an equivalence ratio of 0.55. Similar trends were observed by JPL (Ref. 11-1) in tests of a single-cylinder CFR engine and a 350 CID V-8 engine.

In tests of the Siemens "catalytic carburetor," a 20 percent improvement in gas mileage (miles per gallon) was reported at operation with 20 percent more air than stoichiometric ($\phi = 0.8$) (Ref. 11-6).

Substantive fuel economy data from vehicle tests are currently not available.

11.2.3 Emissions Effects

The principal driving force behind the development of fuel reformers or hydrogen generators has been the potential for reducing emissions by (1) using a fuel product (hydrogen) having inherently lower exhaust emission products and (2) using a fuel product (hydrogen) enabling very lean engine operation. Lean operation has long been recognized as offering the potential for concurrent or simultaneous reductions of all three exhaust emissions species (HC, CO, NO_x). For the case where all of the fuel consumed by the engine is reformer products (H_2, CO, etc.), data are available for three specific concepts.

As reported in Reference 11-7, tests from a prototype model of the International Materials Corporation reformer in simulated vehicle operation demonstrated CO emissions of 0.412 to 2.78 grams per vehicle miles (gm/mi), unburned hydrocarbons of 0.012 to 0.15 gm/mi, and NO_x of 0.040 to 0.37 gm/mi. References of this type which convert all of the engine's fuel requirements are typically large in volume and pose difficult vehicle packaging problems. In addition, reformer inefficiencies are applied to all of the gasoline used by the vehicle and may result in reduced fuel economy.

Siemens "catalytic carburetor" tests (Ref. 11-6) indicated the following emissions resulted when tested with a small (122 cubic inch) engine:

	Unmodified Engine		Catalytic Carburetor		
	Standard Carb.	Leanest Possible Setting	$\phi = 1$	$\phi = 0.8$	$\phi = 0.7\text{-}0.75$
CO	1.5%	0.5%	0.15%	0.09%	CO went up
NO_x	1,400 ppm	1,200 ppm	1,000 ppm	40 ppm	NO_x went down further

No hydrccarbon emissions data were presented in Reference 11-6.

Emissions were also measured in the Phillips Petroleum Company CFR tests of gasoline and synthetic normal hexane reformate fuels noted above in Section 11.2.2 (Ref. 11-2). These tests gave the following results in terms of weighted average emissions over a simulated driving schedule (Ref. 11-10) for optimum spark timing, and homogeneous, lean, fuel-air mixtures:

	Reformate Fuel Only	Gasoline Only
Carbon monoxide, gm/ihp-hr	0.8	47.5
Hydrocarbons, gm/ihp-hr	0	3.8
Nitric Oxide, gm/ihp-hr	0.9	6.8

where ihp-hr = indicated horsepower per hour

In the case where only a portion of the fuel used by the engine is passed through the reformer, substantive data are available from recent hydrogen-supplemented gasoline tests performed by General Motors and JPL.

The effect of lean operation on emissions with isooctane-hydrogen mixtures in a single-cylinder engine is shown in Figure 11-11 (from Ref. 11-9). As was the case with pure hydrogen, NO_x emission was extremely low for equivalence ratios leaner than 0.55. The 0.55 equivalence ratio is then an apparent optimum mixture, since NO_x emission was reduced to near-minimum

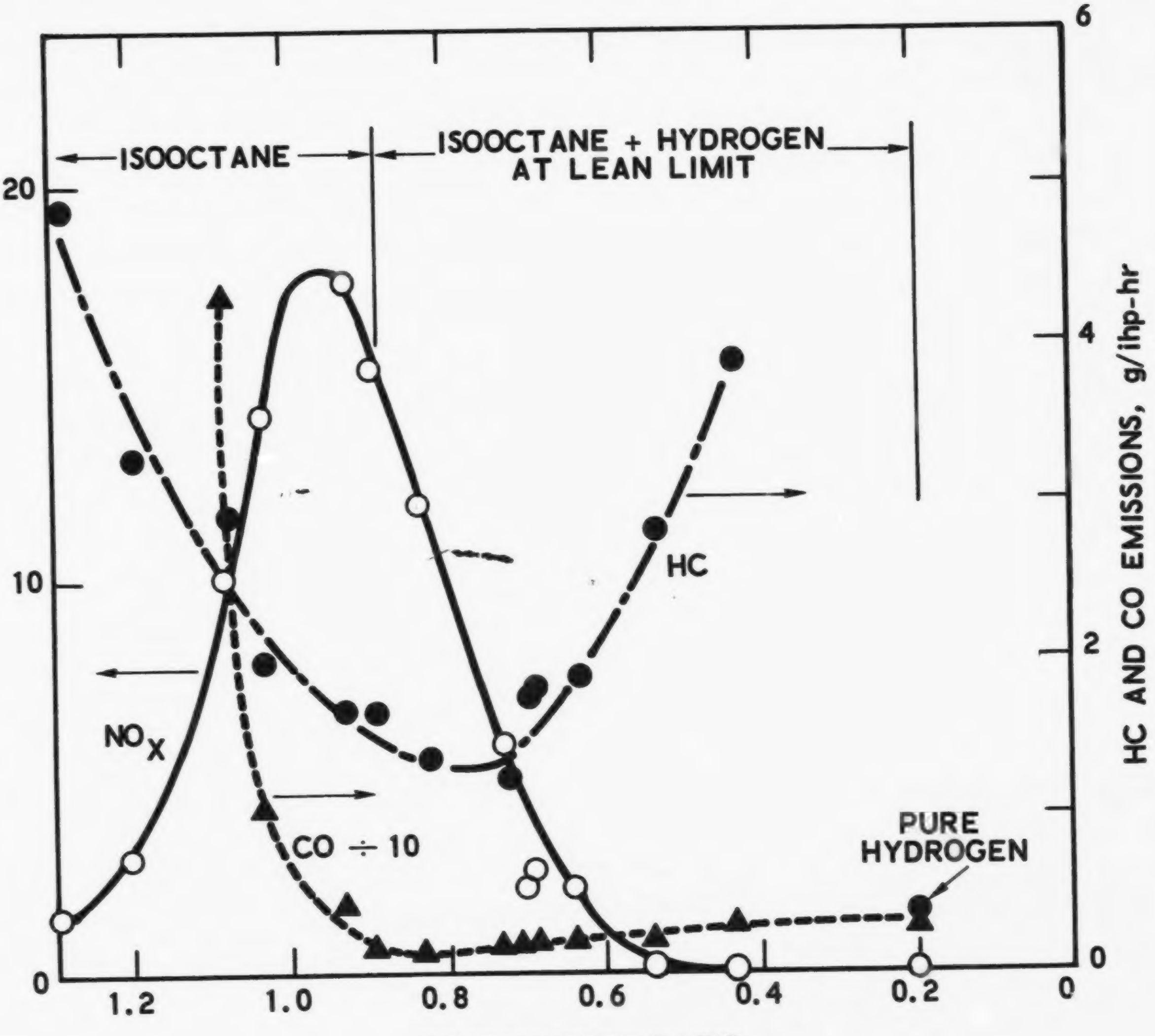

Figure 11-11. Emissions Characteristics of Isooctane-Hydrogen Fuel Mixtures (Ref. 11-9)

levels with limited hydrogen requirement. However, as is typical of extremely lean operation on hydrocarbon fuels, the HC emission increased with very lean mixtures reflecting the increased quench layer thickness and reduced post-flame oxidation of the quenched hydrocarbons. At 0.55 equivalence ratio, HC emission increased about 100 percent from the minimum level. In contrast, the leaner operation made possible by hydrogen addition had only a minor effect on CO emission; CFR and V-8 engine (350-CID) tests by JPL (Ref. 11-1) with hydrogen-plus-gasoline mixtures exhibited results and trends generally similar to the General Motors data of Figure 11-11.

Recent JPL comparison tests of a 1973 Chevrolet Impala on the 1975 Federal Test Procedure (FTP) (Ref. 11-5), first with gasoline only and then with hydrogen-supplemented gasoline, produced the following exhaust emissions results:

	Stock Impala (Gasoline only-stock carburetor)	Modified Impala (Gasoline plus hydrogen-special test carburetor)
HC gm/mi	2.29	2.17
CO gm/mi	43.91	1.63
NO_x gm/mi	1.75	0.67

The hydrogen was supplied from hydrogen gas bottles located in the trunk of the car. The variation of equivalence ratio throughout the test is not known. The reduction in CO and NO_x is marked. It should be noted that the special test carburetor used could have effects on the data shown.

In-the-engine control of NO_x was also verified by General Motors in one experimental vehicle tailored to operate at mixture equivalence ratios of 0.55 to 0.65 with a hydrogen fraction of 0.10 for most driving conditions; the hydrogen was again supplied by gas bottles in the trunk of the car. Results of exhaust emissions tests on the cold start 1975 FTP at 3,500-pound inertia weight were as follows:

Vehicle Exhaust Emissions with Constant Hydrogen Fraction (Ref. 11-9)

	Emissions,[*] gm/mi		
	NO_x	CO	HC
	0.34	3.3	3.2
	0.44	3.3	3.0
Average	0.39	3.3	3.1

NO_x and CO satisfied the 0.4 and 3.4 gm/mi standards, respectively. Hydrocarbon emission, however, was nearly an order of magnitude higher than the 0.41 gm/mi limit.

All of the foregoing tests were initial exploratory tests and may not reflect ultimate system potential for engines operated on reformed fuel nor for the case of gasoline supplemented by either hydrogen or reformed fuel.

11.2.4 Toxicity Effects

The principal ingredients in gaseous reformed fuel products are hydrogen, carbon monoxide, and water vapor, as delineated in Section 11.1.4; other ingredients which may be present include methane, carbon dioxide, and other unreacted hydrocarbons. A brief resume of the toxicity effects of the various ingredients follows:

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[*] 1975 Federal Test Procedure

- Hydrogen. Acts as a simple asphyxiant; decreases available oxygen; no warning properties (see Section 8.2.4)
- Carbon monoxide. A colorless, ordorless gas; very poisonous
- Water. Nontoxic
- Methane. Toxicity ranges from none to slight; less toxic than gasoline (refer to Table 5-3)
- Carbon dioxide. Nontoxic
- Unreacted hydrocarbons. Similar to gasoline (Section 3.2.3.1): low oral toxicity; low dermal toxicity; significant aspiration effects (minute amounts drawn into lungs can be rapidly fatal).

11.2.5 Safety Effects

With regard to on-board storage of the liquid hydrocarbon fuel prior to reformation, the safety hazards should be similar to those of current fuels and would depend on the specific fuel used. Fire and explosion would be the principal hazards for the lower boiling fractions such as gasoline. Higher boiling fuels, such as diesel and fuel oils, only represent a fire hazard due to their lower volatility.

When the reformer is in operation, the generation of gaseous products could introduce the additional hazard of fires if lines or pressure vessels leak or rupture due to the hydrogen content of the reformer products (see Section 8.2.5.1).

If an accumulator is used in the system to store reformed fuel products (for example, for starting on gaseous fuel products), additional hazards of vessel rupture, fire, and explosives are introduced, with the degree of hazard associated with the level of pressure at which the products are stored.

11.2.6 Handling, Storage, and Distribution

All of the liquid hydrocarbon fuels that are potential candidates for use with fuel reformers are in commercial use today with contemporary handling, storage, and distribution systems. This fact enhances the potential for use of reformed fuel systems, since no new handling, storage, or distribution systems would be required.

11.2.7 Critical Research Gaps

Although a number of investigators (Refs. 11-1 through 11-9) have made available selected data that tend to confirm that fuel reformation (partial or total) can beneficially reduce exhaust emissions and/or increase fuel economy (via lean operation), there is no single comprehensive set of experimental and/or analytical data for any given concept which fully treats the combined effects of emissions, fuel economy, power loss, and system operation to the degree necessary to fully evaluate the concept potential. Principal data missing or factors not adequately treated or assessed include:

a. Techniques for reducing high HC emission levels during lean operation
b. Actual emission levels for all constituents (HC, CO, and NO_x) when actual reformer products are burned in the engine (H_2 plus gasoline mixtures and synthesized reformer products used in most cases to date)
c. Experimental determination of fuel reformer output and performance in a finite and reasonable size (e.g., as would be built for installation in a passenger car for production)
d. Measurement of fuel economy with an actual reformer system operating in a vehicle driven over the Federal Driving Cycle
e. Determination of the operating characteristics of the reformer/engine system over the full range of normal vehicle operation
f. The reformer/vehicle performance capability over the full range of normal vehicle operation in customer use, including speed and load conditions not encountered in the Federal Driving Cycle
g. The effect of high-temperature reformer products on engine performance
h. Potential soot formation problems
i. Water handling and attendant problems (volume, weight, location, freezing, vehicle weight, growth effects, etc.)
j. System startup and control techniques
k. Overall system economics and durability.

11.3 CURRENT STATUS

No mobile on-board fuel reformer system is known to be in developmental vehicle operation. A prototype model of the International Materials Corporation concept reformer has been operated on a chassis dynamometer (Ref. 11-7). The Siemens "catalytic carburetor" concept is reported to have been under study for some years, with recent engine dynamometer tests on a small (122-cubic inch) engine and a larger 170-horsepower engine (Ref. 11-6); and JPL has performed reformer tests with an experimental laboratory reformer unit and a 350-CID V-8 engine in an engine dynamometer, but their passenger car tests (1973 Chevrolet Impala) have been restricted to tests with gasoline supplemented by gaseous hydrogen. Available data on the Phillips catalytic reformer concept are restricted to CFR engine tests with synthesized reformate fuel products only (Ref. 11-2).

In summary, with regard to current status, fuel reformer concepts are still in the exploratory, proof-of-principle, or feasibility determination stage. A number of critical data gaps exist, as delineated in Section 11.2.7, which must be filled before on-board reformed fuels can be fully assessed as to their future potential. NASA has been funding the Jet Propulsion Laboratory to acquire data and prove concept feasibility and EPA is providing supplemental funding for this work in addition to other contractor-supported programs for evaluation of similar concepts.

11.4 PROJECTED STATUS

11.4.1 Availability

Since fuel reformer concepts have the potential to operate with a wide range of liquid hydrocarbon fuels (Section 5.9.1.2), the concept is limited as to fuel reserves and/or raw material sources only insofar as conventional petroleum or nonpetroleum hydrocarbon fuels are limited (see Sections 3, 4, and 7). The availability of on-board reformed fuels is limited by the availability of a developed fuel reformer system which can be mass produced and marketed on a competitive basis with other engine systems competing for the same liquid hydrocarbon basic fuel source. As noted in

Section 11.3, such a reformer system has not yet reached the prototype vehicle demonstration stage.

11.4.2 Projected Consumer Costs

Estimates of consumer initial costs for mass-produced fuel reformers have not yet been made available in the literature. Maintenance cost requirements are similarly not available. If fuel reformer use results in full economy gains (as postulated), then the consumer will realize fuel cost savings.

11.4.3 Capital Costs and Timing Implications

As in the case of initial consumer costs, no estimates of capital cost requirements are available. However, by analogy with emission control system concepts such as thermal reactors and catalytic converters, it would take the automobile industry at least three to four years after successful prototype vehicle evaluation to produce reformer systems in any sizeable mass-production quantities.

11.4.4 Impact with Other U.S. Energy Requirements

The fuel reformer concept, per se, should have no adverse impact on other U.S. energy requirements, but will not alleviate future shortages of gasoline or distillates. One possible attribute advanced for this broad concept is that it may be compatible with the use of a number of basic hydrocarbon fuels over a wide boiling range. However, specific reformer designs may require the use of a single fuel grade in order to operate most efficiently. For those concepts that reform only a portion of the engine's fuel requirements for the conventional spark ignition engine, the fuel choice would, of course, be limited to gasoline.

11.4.5 Factors Which May Inhibit Use

Assuming that reformer system performance (emissions and fuel economy) goals can be met, there are a number of other factors which could inhibit their use. Chief among these may be:

- Reformer system installation size

- Reformer system operational complexity
- High system installed cost
- Potential of soot production (partial oxidation systems)
- High engine power losses (causing increased engine displacement and size and weight for same output)
- Water storage and freezing problems.

11.4.6 Critical Technology Gaps

Although a number of general and specific research data gaps were identified as being critical to the overall assessment of the reformed fuel system concept (Section 11.2.7), the fuel reformer device itself is the critical technology gap. Research and development efforts are required, for a specific reformer device, to demonstrate adequate lifetime and performance characteristics, including transient output characteristics and control system compatibility with the engine/vehicle system.

11.4.7 Potential for National and Regional Use

Due to the present lack of demonstration of concept feasibility (on an overall system basis), the application of on-board fuel reformers to automotive systems does not seem to be immediately pending. As previously noted, extensive research and development efforts are required to resolve uncertainties as to reformer, reformer/engine, and engine/vehicle system performance potential and exhaust emission and fuel economy characteristics.

The effectiveness of hydrogen-supplemented fuel in extending lean operating limits and reducing NO_x and CO emissions has been substantiated in single-cylinder-engine tests and in experimental vehicles modified to carry on-board gaseous hydrogen storage bottles. When 10-percent hydrogen (by weight) was used, engine power decreased by approximately 40 percent, and indicated thermal efficiency increased from 33 percent to 37 percent. Hydrocarbon emissions were increased, as is typical of very lean combustion engines operating with hydrocarbon fuels.

ABBREVIATIONS

ACGH	American Congress of Government Hygenists
AGA	American Gas Association
APHA	American Public Health Association
atm	atmosphere
bbl	barrel
btdc	before top dead center
BuMines	Bureau of Mines
C_2H_5OH	chemical formula for ethyl alcohol or ethanol
C_3H_6O	chemical formula for acetone
C_6H_6	chemical formula for benzene
CFR	Cooperative Fuel Research (Council)
CH_3OH	chemical formula for methyl alcohol or methanol
CH_4	chemical formula for methane
CNG	compressed natural gas
C_6H_{12}	chemical formula for cyclohexane
CO	chemical formula for carbon monoxide
CO_2	chemical formula for carbon dioxide
CR	compression ratio
CSF	Consol Synthetic Fuel
CVS	constant volume sampling (federal test procedure)
DCF	Discounted Cash Flow, a method of computing return on investment

EGR	exhaust gas recirculation
ft^2	square foot
ft^3	cubic foot
Fe	chemical symbol for iron
f.o.b.	free on board
FTP	Federal Test Procedure
FPC	Federal Power Commission
g, gm	gram
GSA	General Services Administration
H_2	chemical formula for hydrogen
H_2O	chemical formula for water
HHV	higher heating value (see Glossary)
HIT	hydrogen induction technique
HOAc	a procedure for measuring acidity
IBP	initial boiling point
ICC	Interstate Commerce Commission
IGT	Institute of Gas Technology
IMEP	indicated mean effective pressure
ISFC	indicated specific fuel consumption
JPL	Jet Propulsion Laboratory
$KMnO_4$	chemical formula for potassium permanganate
KOH	chemical formula for potassium hydroxide
kW-hr	kilowatt (thousand watts) hour
lb	pound(s)
LHV	lower or net heating value (see Glossary)

LNG	liquified natural gas
LTA	lighter than air(craft)
M	thousand
ml	milliliter
MM	million
MMCF	million cubic feet
MSCF	thousand standard cubic feet
mol	molecule
MON	motor octane number
MW	megawatt (million watts)
N_2	chemical formula for nitrogen
N_2H_4	chemical formula for hydrazine
NG	natural gas
NGL	natural gas liquids
NH_3	chemical formula for ammonia
Ni	symbol for nickel
O_2	chemical formula for oxygen
PGC	Potential Gas Committee
ϕ (phi)	equivalence ratio
ppm	parts per million
psi	pounds per square inch
psia	pounds per square inch absolute
Pu	symbol for plutonium
ROI	return on investment

RON	research (or road) octane number
Ru	symbol for ruthenium
SAE	Society of Automotive Engineers
SCF	standard cubic foot (of gas) measured at 70° F and 14.696 psia
ST	stream day
SFC	specific fuel consumption
SNG	synthetic natural gas
SRC	solvent refined coal
ST	short ton, 2,000 pounds
tel	tetra-ethyl lead
ThO_2	chemical symbol for thorium oxide
T/SD	tons per stream day
UCLA	University of California, Los Angeles
U	symbol for uranium
U.S.B.M.	United States Bureau of Mines
USI	United States Industries
w/o	without
WOT	wide open throttle
ZnO	chemical formula for zinc oxide

GLOSSARY

aldehyde	an odorous, oxygenated hydrocarbon classified as a pollutant
anhydrous	without water
°API	a method of expressing specific gravity for hydrocarbon fuels $^\circ\mathrm{API} = \frac{141.5}{\text{specific gravity of hydrocarbon}} - 131.5$ specific gravity for test fluid referenced to water at 60°F.
catalyst	a substance that increases the rate of a chemical reaction without itself undergoing a permanent chemical change
cetane number	a measure of the ignition delay of a fuel in a compression ignition (diesel) engine
cryogenic	related to the production and effects of very low temperatures
endothermic reaction	a chemical reaction in which heat is absorbed
equivalence ratio	the actual fuel-air ratio to stoichiometric fuel-air ratio
exothermic reaction	a chemical reaction in which heat is evolved
fixed-bed reactor	a grate or bed in which pellets are tightly packed and constrained from movement as a hot gas stream flows through the bed
flash point	the temperature at which the vapor above bulk liquid can be ignited by an open flame
fluidized-bed reactor	a grate or bed in which finely divided pellets are free to move in the vertical direction and are suspended by the upward flow of a hot gas stream
gross or higher heating value (HHV)	the energy released by a fuel when it is completely burned in such a way that the water vapor of combustion is condensed to a liquid

hypergolic ignition	spontaneous ignition upon contact of the fuel and oxidizer
hydrocracking	catalytic cracking process with simultaneous hydrogenation used in the processing of crude oil
kerogen	bituminous material occuring in shale and yielding oil when heated
kinematic viscosity	viscosity divided by density
methanol	same as methyl alcohol
naphtha	a light oil product of petroleum having properties intermediate between gasoline and kerosene
natural gas	a gaseous fuel consisting primarily of methane
neat	a pure material without additives
net or lower heating value (LHV)	the energy released by a fuel when it is burned completely without condensing the water vapor of combustion
octane number	a measure of the resistance of a fuel to detonate in a spark ignition, reciprocating (Otto cycle) engine
photovoltaic	relating to the generation of an electromotive force when radiant energy falls on the boundary of dissimilar substances
pyrolysis	chemical decomposition resulting from heat in the absence of oxygen
Rankine engine	a heat engine that operates in the Rankine thermodynamic cycle, which includes fluid vaporization, expansion, and condensation stages (e.g., conventional steam engine)
recuperator	a fixed device used to improve gas turbine engine efficiency by providing for heat exchange between turbine exhaust gases and compressor outlet air
regenerator	a rotating device used to improve gas turbine engine efficiency by providing for heat exchange between turbine exhaust gases and compressor outlet air
regenerative engine	incorporates a regenerator or recuperator to improve engine efficiency

specific fuel consumption	fuel consumption of a heat engine measured in terms of fuel weight per hour consumed by the engine divided by its horsepower output
stoichiometric	refers to conditions in a combustion process wherein the fuel is completely burned with no excess oxygen remaining
syncrude	a synthetic crude oil made from oil shale or coal
thermal efficiency	the ratio of theoretical work done by an engine to the mechanical equivalent of heat supplied in the fuel
thermal reforming	a process using heat (but no catalyst) to effect molecular rearrangement of a hydrocarbon fuel (example: low-octane naphtha into gasoline of higher antiknock quality)

REFERENCES

1-1. Walter G. Dupree and James A. West, *United States Energy Through the Year 2000*, U.S. Department of the Interior, Washington, D.C. (December 1972).

2-1. *Feasibility Study of Alternative Fuels for Automotive Transportation-Phase I*, Institute of Gas Technology; preliminary information, EPA Contract 68-01-2111, September 1973-May 1974; report to be published.

2-2. *U.S. Energy Outlook*, National Petroleum Council (December 1972).

2-3. *Energy: Uses, Sources, Issues*, Lawrence Livermore Laboratory (30 May 1972).

2-4. Thomas H. Mangh II, "Fuel from Wastes: A Minor Energy Source," *Science* *I* (78) (10 November 1972).

2-5. L. L. Anderson, *Information Circular 8549*, Bureau of Mines, (1972), p. 13.

2-6. H. R. Linden, "Review of World Energy Supplies," IGT 12th World Gas Conference, Nice, June 1973.

2-7. A. C. Mailliaris and R. L. Strombotne, "Demand for Energy by the Transportation Sector and Opportunities for Energy Conservation," U.S. Department of Transportation, *1973 Conference at MIT on Energy: Demand, Conservation and Institutional Problems*.

2-8. N. E. Fraize, *U.S. Transportation - Some Energy and Environmental Considerations*, M72-164, The Mitre Corporation (September 1972).

2-9. *Oil and Gas Journal*, Petroleum Publication Company, Tulsa, Oklahoma (12 March 1973).

3-1. *Clean Energy from Coal - A National Priority*, Annual Report of the Office of Coal Research, U.S. Department of Interior (February 1973).

3-2. *Feasibility Study of Alternative Fuels for Automotive Transportation - Phase I*, Institute of Gas Technology; Preliminary Information, EPA Contract 68-01-2111, September 1973-May 1974; report to be published.

3-3. W. W. Bodle and K. C. Vyas, "Clean Fuels from Coal, Introduction to Modern Processes," presented at the Clean Fuels from Coal Symposium, Institute of Gas Technology, Chicago, Illinois, 10-14 September 1973.

3-4. *Chemical and Engineering News*, p. 19 (26 November 1973).

3-5. H. C. Hottel and J. B. Howard, *New Energy Technology - Some Facts and Assessments*, The MIT Press, Cambridge, Mass. (1971).

3-6. *Feasibility Study of Alternative Fuels for Automotive Transportation - Phase I*, Esso Research and Engineering Company; preliminary information as of January 1974; report to be published.*

3-7. *Feasibility Study of Alternative Fuels for Automotive Transportation - Phase I*, Esso Research and Engineering Company; preliminary information as of November 1973; reported to be published.*

3-8. "U.S. Energy Outlook," National Petroleum Council (December 1972).

3-9. C. A. Johnson, et al., "Present Status of the H-Coal Process," Clean Fuels from Coal Symposium, Institute of Gas Technology, Chicago, Illinois, 10-14 September 1973.

3-10. M. E. Frank and B. K. Schmid, "Economic Evaluation and Process Design of a Coal-Oil-Gas (COG) Refinery," Clean Fuels from Coal Symposium, Institute of Gas Technology, Chicago, Illinois, 10-14 September 1973.

3-11. G. V. Dinneen and L. Cook, "Oil Shale and the Energy Crisis," ASME Paper 72-WA/FU-3 (1972).

3-12. *Chemical and Engineering News*, p. 60 (29 October 1973).

4-1. Kirk-Othmer, *Encyclopedia of Chemical Technology*, Vol. 13, 2nd Ed., John Wiley and Sons, (1963), pp 370-398.

4-2. J. C. Hoogendoorn, "Experience with Fischer-Tropsch Synthesis at Sasol," Clean Fuels from Coal Symposium, Institute of Gas Technology, Chicago, Illinois, 10-14 September 1973.

4-3. G. C. Szego, et al., "The Energy Plantation," Intersociety Energy Conversion Engineering Conference, 1972.

---

*Preliminary information has been updated subsequent to publication of Exxon final report: F. H. Kant, et al., *Feasibility Study of Alternative Fuels for Automotive Transportation* (in three volumes), EPA-460/3-74-009-4-a, Exxon Research and Engineering Company (June 1974).

4-4. Kirk-Othmer, Encycopedia of Chemical Technology, Vol. 22, 2nd Ed., John Wiley and Sons, (1963), p. 382.

4-5. W. R. Cherry, "Harnessing Solar Energy: The Potential," Astronautics and Aeronautics 11 (8) (30 August 1973).

4-6. "Low Pressure Route to Methanol," Oil and Gas Journal, p. 35 (12 March 1973).

4-7. J. Bolt,"A Survey of Alcohol as a Motor Fuel," SAE Preprint SP-254 (1964).

4-8. E. S. Starkman, H. K. Newhall, and R. D. Sutton, Comparative Performance of Alcohol and Hydrocarbon Fuels, SAE Preprint SP-254 (1964).

4-9. G. D. Ebersole and F. S. Manning, Engine Performance and Exhaust Emissions: Methanol vs Isooctane, SAE Preprint No. 720692 (August 1972).

4-10. "Use of Alcohol in Motor Gasoline - A Review," American Petroleum Institute, Publication 4082 (August 1971).

4-11. R. E. Fitch and J. D. Kilgroe, Investigation of a Substitute Fuel to Control Automotive Air Pollution, Final Report CETEC 01800-FR, Consolidated Engineering Technology Corporation (February 1970).

4-12. R. K. Pefley, M. A. Saad, M. A. Sweeney, and J. D. Kilgroe, Study of Decomposed Methanol as a Low Emission Fuel, Final Report - Contract EHS 70-118 NAPCA, University of Santa Clara (April 1971).

4-13. H. G. Adelman, D. G. Andrews, R. S. Devoto, Exhaust Emissions from a Methanol-Fueled Automobile, SAE Preprint No. 720693 (August 1972).

4-14. J. S. Ninomiya, A. Golovoy and S. S. Labana, "Effect of Methanol on Exhaust Composition of a Fuel Containing Toluene, n-Heptane, and Isooctane," Journal Air Pollution Control Association 20 (5) 314 (May 1970).

4-15. T. B. Reed and R. M. Lerner, "Methanol: A Versatile Fuel for Immediate Use," Science 182 (4119) 1299 (28 December 1973).

4-16. Feasibility Study of Alternative Fuels for Automotive Transportation - Phase I, Esso Research and Engineering Co.; preliminary information as of January 1974; report to be published.*

---

*See footnote, page R-2

4-17. E. V. Anderson, "Methanol Fortunes Take Turn for Better," Chem. and Eng. News, p. 8 (9 October 1972).

4-18. "Statistical Summary 1973," Supplement to Chemical Statistacs Handbook, 7th Ed., Manuf. Chemists Assoc. (September 1973).

4-19. Feasibility Study of Alternative Fuels for Automotive Transporation - Phase I, Institute of Gas Technology; preliminary information, EPA Contract 68-01-2111, September 1973-May 1974; report to be published.

4-20. Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 13, 2nd Ed., John Wiley and Sons, (1963), p. 395.

4-21. J. C. Davis, "Can Methanol Fuel Contend?" Chemical Engineering, p. 48 (25 June 1973).

4-22. B. M. Bare and H. W. Lambe, "Economics of Methanol," Chem. Eng. Prog. 64 (5) 23 (May 1968).

4-23. B. Hedley, et al., "Methanol: How, Where, Who -- Future," Hydrocarbon Processing, p. 275 (September 1970).

4-24. "Energy Imports: LNG vs MeOH," Chemical Engineering, pp. 233-238 (12 November 1973).

5-1. S. A. Bressler, "Substitute Natural Gas: Processes, Equipment, Costs," Chemical Engineering (16 October 1972).

5-2. "U.S. Energy Outlook," National Petroleum Council (December 1972).

5-3. T. H. Maugh, "Gasification: A Rediscovered Source of Clean Fuel," Science 178 (6 October 1972).

5-4. A. Liversage, "Not Enough Gas in the Pipelines," Fortune (November 1969).

5-5. Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 10, 2nd Ed., John Wiley and Sons (1966), pp. 454-456.

5-6. Kirk-Othmer, Encyclopedia of Chemical Technology, Supplemental Volume, John Wiley and Sons (1971) p. 426.

5-7. H. R. Linden, The Role of SNG in the U.S. Energy Balance, Special Report for the Gas Supply Committee of the AGA (15 May 1973).

5-8. J. J. Brogan, "Present and Future Trends in Automotive Fuel Consumption," Automotive Engineering 81 (7) (July 1973).

5-9. "Cal Tech Clean Air Car Project," Gaseous Fuels Manual, California Institute of Technology (March 1972).

5-10. R. W. McJones and R. J. Corbell, "Natural Gas Fueled Vehicles - Exhaust Emission and Operational Characteristics," Society of Automotive Engineers, Automotive Engineering Congress, January 1970.

5-11. N. E. Fraize, U.S. Transportation - Some Energy and Environmental Considerations, M72-164, The Mitre Corporation (September 1972).

5-12. R. D. Fleming and J. R. Allsup, Natural Gas as an Automotive Fuel, An Experimental Study, U.S. Department of Interior, Report of Investigation-7806 (1973).

5-13. W. D. Anderson, "R&D for Fuel Economy in Automotive Propulsion," U.S. Army Tank-Automotive Command (19 June 1972).

5-14. M. R. Engler, Jr., "Investigation of Liquefied Natural Gas as an Engine Fuel, 69-WS/DGP-3, ASME Meeting, Los Angeles, California November 1969.

5-15. D. B. Eccleston, el al., Clean Automotive Fuel, Engine Emissions Using Natural Gas, Hydrogen-Enriched Gas and Gas Manufactured from Coal (Synthane), TPR 48, U.S. Department of Interior, Bureau of Mines, Salt Lake City, Utah (February 1972).

5-16. W. D. Trammel, "The Energy Crisis and the Chemical Industry," Chemical Engineering (30 April 1973).

5-17. IGT Hygas Process, Institute of Gas Technology brochure (1972).

5-18. R. P. Cahn, et al., Feasibility Study of Alternative Fuels for Automotive Transportation - Phase I, Esso Research and Engineering Co.; preliminary information as of October 1973; report to be published.*

6-1. Bland and Davison, Petroleum Processing Handbook, McGraw-Hill Book Company (1967).

6-2. "Metals, Minerals and Fuels," 1970 Minerals Year Book, Vol. I.

6-3. Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 12, John Wiley and Sons (1967).

---

*See footnote, page R-2

6-4. R. C. Lee and D. B. Wimmer, "Exhaust Emission Abatement by Fuel Variations to Produce Lean Combustion," SAE Paper No. 580769, given at National Fuels and Lubrications Meeting, Tulsa, Oklahoma, 29-31 October 1968.

6-5. *Control Strategies for In-Use Vehicles*, U.S. Environmental Protection Agency (November 1972).

6-6. Fleming, et al., "Propane as an Engine Fuel for Clean Air Requirements," U.S. Department of the Interior, Bureau of Mines, July 1971.

6-7. *Federal Register* *36* (128) pt II (2 July 1971).

6-8. U.S. Environmental Protection Agency, unpublished data, October 1971.

6-9. *Facts and Figures on the Clean Air Question*, booklet, Petrolane, Long Beach, Calif. (1971).

6-10. J. C. Thompson, *NAPCA Findings on Gaseous Fuels*, National Air Pollution Control Administration (October 1970).

6-11. *1971 LP-Gas Market Facts*, National LP-Gas Association.

6-12. Dr. Leo Garwin, "LP-Gas Supplies for the Engine Fuel Market," paper given at the LP-Gas Engine Fuel Symposium, 21-22 October 1970.

7-1. Kirk-Othmer, *Encyclopedia of Chemical Technology*, Vol. 8, 2nd Ed., John Wiley and Sons, pp. 422-427 (1963).

7-2. G. C. Lawreson and P. F. Finigan, *Ethyl Alcohol as a Modern Motor Fuel*, SAE Reprint SP-254 (1964).

7-3. E. L. Kilayko, *Ethyl Alcohol as Fuel for Internal Combustion Engines*, Massachusetts Institute of Technology (August 1960).

7-4. M. W. Jackson, *Exhaust Hydrocarbon and Nitrogen Oxide Concentrations with an Ethyl Alcohol Gasoline Blend*, SAE Preprint SP-254 (1969).

7-5. "Use of Alcohol in Motor Gasoline -- a Review," *American Petroleum Institute*, Publication No. 4082 (August 1971).

8-1. A. F. Bush and W. D. Van Vorst, "On the UCLA Hydrogen Car," School for Engineering and Applied Science, UCLA.

8-2. Hydrogen and Other Synthetic Fuels, Report No. UC-80, U.S. Atomic Energy Commission, Div. of Reactor Development and Technology (September 1972).

8-3. Liquid Propellant Manual, Liquid Propellant Information Agency, LPM-1 (March 1961).

8-4. J. E. Johnson, The Economics of Liquid Hydrogen for Air Transportation, Union Carbide Corporation (10 August 1973).

8-5. R. E. Billings and F. E. Lynch, "History of Hydrogen-Fueled Internal Combustion Engines," Energy Research 73001.

8-6. K. H. Weil, "The Hydrogen IC Engine - Its Origins and Future in the Emerging Energy..."

8-7. R. R. Adt, Jr., D. L. Hershberger, T. Kartage, and M. R. Swain, "The Hydrogen-air Fueled Automobile Engine (Part 1)," School of Engineering and Environmental Design, University of Florida.

8-8. Wall Street Journal (3 August 1965).

8-9. Nitrogen (1964).

8-10. D. H. Stormont, Oil Gas Journal 63 (14) 103-106 (1965).

8-11. R. M. Reed, Trans. American Institute Chemical Engineers 42 (2) 379-401 (1946).

8-12. "Hydrogen: Synthetic Fuel of the Future," Science 178, 849-852 (24 November 1972).

8-13. "Production Figures and Cost Estimates for Fuels," Institute of Gas Technology letter, 27 November 1973.

8-14. "Hydrogen: Likely Fuel of the Future," Chemical and Engineering News, pp. 14-17 (26 June 1972).

8-15. "Hydrogen Fuel Economy: Wide-Ranging Changes," Chemical and Engineering News, pp. 27-30 (10 July 1972).

8-16. Feasibility Study of Alternative Fuels for Automotive Transportation - Phase I, Esso Research and Engineering Co.; preliminary information as of October 1973; report to be published.*

9-1. B. L. Shaw, Inorganic Hydrides, Pergamon Press, Oxford, England (1967).

---

*See footnote, page R-2

9-2. B. S. Hopkins, et al., Essentials of General Chemistry, D. C. Heath & Co., Boston (1946).

9-3. "Ammonia Synthesis from Natural Gas or Naphtha," Oil and Gas Journal (12 March 1973).

9-4. Hydrogen and Other Synthetic Fuels, Synthetic Fuel Panel Report UC-80, Federal Council on Science and Technology (September 1972).

9-5. D. Gregory, "The Hydrogen Economy," Scientific American 228 (January 1973).

9-6. Liquid Propellant Manual Unit 15, Liquid Propellants Information Agency, Johns Hopkins University, Silver Springs, Maryland, (December 1961).

9-7. H. K. Newhall, et al., "Theoretical Performance of Ammonia as a Gas Turbine Fuel," Society of Automotive Engineers Transactions, (17-21 October 1966).

9-8. D. T. Pratt, el al., "Gas Turbine Combustion of Ammonia," Intersociety Energy Conversion Engineering Conference, 1967.

9-9. E. S. Starkman, et al., "Ammonia as a Diesel Engine Fuel: Theory and Application," Society of Automotive Engineers Transactions, Paper 660768 (1967).

9-10. E. S. Starkman, et al., "Flame-Propagation Rates in Ammonia-Air Combustion at High Pressure," Eleventh Symposium on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania, 1967.

9-11. H. W. Cremer, et al., Chemical Engineering Practice, Vol. 10, Academic Press, Inc., New York (1960).

9-12. E. S. Starkman, et al., "Ammonia as a Spark Ignition Engine Fuel: Theory and Application," given at Intersociety Energy Conversion Engineering Conference, 1966.

9-13. Feasibility Study of Alternative Fuels for Automotive Transportation - Phase I, Esso Research and Engineering Co.; preliminary information as of September 1973; report to be published.*

9-14. Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 2, 2nd Ed., John Wiley and Sons, Inc. (1963).

9-15. "1971, A Subpar Year for Chemical Production, But Fibers, Plastics, Fertilizers Made Gains," Chemical and Engineering News (5 June 1972).

---

*See footnote, page R-2

9-16. Oil and Gas Journal (12 March 1973).

9-17. L. W. Westerstrom, "Coal-Bituminous and Lignite," Minerals Yearbook (1970).

9-18. Environmental Effects of Producing Electric Power, Joint Committee on Atomic Energy Congress of the U.S. Hearings, October - November 1969.

9-19. "Coal Gasification; Can it Stage a Comeback," Chemical Engineering (3 April 1972).

9-20. Cost Engineering in the Process Industries, McGraw-Hill Book Co., New York (1960), p. 282.

9-21. R. E. Blanco,et al., "Ammonia Cost and Electricity," Chemical Engineering Progress (April 1967).

10-1. Kirk Othmer, "Hydrazine," Encyclopedia of Chemical Technology, Vol. 2, 2nd Ed., John Wiley and Sons, pp. 164-196.

10-2. "Hydrazine," Liquid Propellant Manual, Unit 2, Liquid Propellant Information Agency (March 1961).

11-1. Breshears, Cotrill, and Rupe, Partial Hydrogen Injection into Internal Combustion Engines Effect on Emissions and Fuel Economy, First Symposium on Low Pollution Power Systems Development, Ann Arbor, Michigan (14-19 October 1973).

11-2. Method and Apparatus for Reducing Engine Exhaust Pollutants, United States Patent 3,717,129 (20 February 1973).

11-3. Method and Means for Generating Hydrogen and a Motive Source Incorporating Same, United States Patent 3,682,142 (8 August 1972).

11-4. Marc S. Newkirk and James L. Abel, The Boston Reformed Fuel Car, International Materials Corp., SAE Paper No. 720670 (2 November 1971).

11-5. S. R. Breshears, "Partial Hydrogen Injection Into Internal Combustion Engines Effect on Emissions and Fuel Economy," Project briefing at Jet Propulsion Laboratory (February 1974).

11-6. "Siemens Catalytic Carburetor Gives Cleaner Exhaust," Popular Science Magazine, pp. 76-77 (December 1973).

11-7. Machine Design, p. 42 (9 April 1973).

11-8. Personal communication with JPL personnel.

11-9. R. F. Stebar and F. B. Parks, "Emission Control with Lean Operation Using Hydrogen Supplemented Fuel," SAE Paper No. 740187, General Motors Research Laboratories (25 February - 1 March 1974).

11-10. "Los Angeles Traffic Pattern Survey," Vehicle Emission SAE Progress Series 617, Macmillan Co. (1964).